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# Amphifunctionally Electrified Interfaces: Coupling of Electronic and Ionic Surface-Charging Processes

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Solid/liquid interfaces can acquire a charge by two principally different processes, i.e., by charging the interface via an external electric source or by specific adsorption/desorption of ionic species from/to the liquid. Here, we analyze the properties of electric double layers (DL) that are governed by the simultaneous functioning and coupling of these two charging mechanisms. For such interfaces, which we will denote as amphifunctional, the quantitative dependencies of the DL parameters on the electric variables and bulk composition are computed. The interface between a partially oxidized metal and an electrolyte solution is an example of an amphifunctional interface. Particular situations occur at the point of zero charge (pzc) and at the isoelectric point, which refer to specific values of the electrode potential and the pH of the solution. Limiting cases of the amphifunctional model correspond to the familiar DL behavior of either fully polarized metal/electrolyte interfaces or fully relaxed oxide/electrolyte interfaces. Our analysis can successfully be applied in the interpretation of recent atomic force microscopy force measurements on the gold/solution interface. It also allows a new approach in the understanding of the dependence on pH of the potential of zero charge of metals and the dependence on the potential of pzc (pH value) of oxide surfaces.

## Introduction

For solid/solution interfaces, generally, two principally different charging processes can be distinguished.

(i) A double layer (DL) can be imposed externally. Over the range of potentials applied across the interface where no faradaic current flows, the interface is called “polarizable”. The classical representative is the mercury/aqueous solution interface. The interfacial tension or the differential DL capacitance can be measured as a function of an externally applied potential. Electrocapillary curves are obtained, which upon differentiation yield the surface charge density.<sup>1,2</sup> It is characteristic for such interfaces that the externally supplied electric energy gives rise to an independent term in the Gibbs adsorption equation.<sup>3</sup>

(ii) A DL can form spontaneously by preferential adsorption/desorption of certain types of ions. Such DLs, denoted as electrically “relaxed” or “reversible”, involve ion exchange equilibria between the surface and the medium. Typical examples are insoluble oxides, which exchange protons with the aqueous medium.<sup>4–6</sup> For these interfaces, the ion excess and the electric components of charge are coupled in the Gibbs equation.<sup>7</sup>

The difference in behavior between electrically relaxed and electrically polarized interfaces is not absolute. Mercury electrodes can become reversible at potentials where a faradaic current flows: that is, when a “depo-

larizer” is present. On the other hand, relaxed interfaces such as at AgI electrodes can be polarized by working at sufficiently high frequencies.<sup>8</sup> The present paper is concerned with interfaces at zero frequency where the two operative processes described in (i) and (ii) jointly determine DL formation. In this case, the surface charge depends on both the pH and the external potential. Our attention will be focused on systems allowing for the coupling of (i) and (ii), the interface between an oxidized metal and an aqueous electrolyte being one of them. This latter interface is often encountered in electrochemistry in fields as disparate as electrocatalysis,<sup>9–12</sup> electrodeposition,<sup>13,14</sup> corrosion,<sup>15,16</sup> and kinetic studies of electroactive species.<sup>17,18</sup> Colloid scientists encounter the full range of metal to metal oxide surfaces in contact with electrolytes. A rigorous analysis of the DL under conditions where both the metallic character and the ion exchange function are included is most timely. Recent atomic force microscopy (AFM) force measurements on such interfaces<sup>19–22</sup> are calling for quantitative interpretation of the DL properties.

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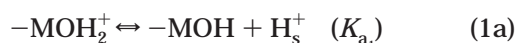
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## 2. Double Layer Properties of Amphifunctional Interfaces

**2.1. Description of the Amphifunctionality of the Systems Considered.** The oxidized metal/electrolyte interface combines features of both relaxed and polarized interfaces, for which we shall now summarize the functional properties. Studies of relaxed oxide/electrolyte interfaces have been carried out in great detail by many authors (e.g., see refs 23–27). The charging processes for such interfaces take place via uptake or release of protons. The substrate exhibits a surface hydration leading to the formation of amphoteric hydroxyl surface groups ( $-\text{MOH}$ ). The resulting surface charge ( $\sigma^0$ ), which we shall call the protonic surface charge, derives from the acid–base interactions of the solution components with these surface groups. The relevant protolytic reactions of the  $-\text{MOH}$  groups are



for which the constants  $K_{a_1}$  and  $K_{a_2}$  ( $K_{a_1} > K_{a_2}$ ) are the measures of their acidity and alkalinity.  $\text{H}_s^+$  denotes a proton close to the surface. If we write the surface concentrations of the various species as  $[-\text{MOH}]$ ,  $[-\text{MO}^-]$ , and  $[-\text{MOH}_2^+]$  in terms of molecules per unit area,  $\sigma^0$  is given by

$$\sigma^0 = e([-\text{MOH}_2^+] - [-\text{MO}^-]) \quad (\text{C m}^{-2}) \quad (2)$$

with  $e$  as the elementary charge.

We can define  $N_s$ , the total number of sites per unit surface area, as

$$N_s = [-\text{MOH}] + [-\text{MOH}_2^+] + [-\text{MO}^-] \quad (\text{m}^{-2}) \quad (3)$$

The ensuing formulation of the variation of  $\sigma^0$  with pH is known as the site-binding model.<sup>28,29</sup> Protons ( $\text{H}^+$ ) and hydroxyl ions ( $\text{OH}^-$ ) may be considered as “charge-determining”. Consequently, the pH of the solution is the primary externally adjustable variable, which together with the electrolyte concentration determines the sign and the magnitude of  $\sigma^0$ . Important characteristics of the amphoteric surface are the isoelectric point (iep) and the point of zero charge (pzc). In the absence of specific adsorption of ions, the iep and the pzc are equal and this pzc is sometimes called the “pristine point of zero charge” (ppzc). For that point, we have

$$\text{iep} = \text{pzc} = \text{ppzc} = (1/2) (\text{p}K_{a_1} + \text{p}K_{a_2}) \quad (4)$$

In practice, the DL at the oxide/solution interface is commonly studied by titration and electrokinetics. From these data, one can estimate the parameters  $K_{a_1}$  and  $K_{a_2}$  as well as  $N_s$  by using some extrapolation procedure mentioned in the literature.<sup>30,31</sup>

For the nonoxidized parts of the metal surface, the surface potential does not depend on pH and is only externally applied. The surface charge depends on this potential and on the presence of specifically adsorbing ions. In practice, potentials are always given with respect to a reference state; therefore, a point of zero potential (pzp) cannot be defined. As for a relaxed interface, one speaks in terms of pzc as a reference state for the electrode surface. This common terminology used for both types of interfaces might induce some confusion since the pzc for a polarized interface refers to a potential, whereas the pzc for a relaxed oxide/solution interface is a pH value. The numerous data reported in the literature and related to the DL at the mercury electrode<sup>32</sup> are mostly derived from the surface tension ( $\gamma$ ) as a function of the applied potential ( $\Delta\varphi$ ). The  $\gamma(\Delta\varphi)$  plots are called electrocapillary curves, which upon differentiation yield the excess charge on the metal  $\sigma^e$ . Electrocapillary curves have a pseudoparabolic shape with a maximum, known as the electrocapillary maximum. At this maximum,  $\sigma^e = 0$ , so that automatically the pzc is obtained.

For amphifunctional interfaces, we allow the solution side of the DL to be determined by the combination of both charge-determining processes mentioned previously. This combination of electric and electrolytic surface-charging elements generates the amphifunctionality. Experimentally, investigation of the amphifunctionality can be achieved either by applying a given potential across the interface (potentiostatic experiments)<sup>19</sup> or by supplying to the conducting phase a known electronic charge (galvanostatic experiment) at constant bulk composition. Once equilibrium is reached, the relationships between electric and electrolytic parameters remain independent of the type of experiments used to build up the DL; that is, the state is independent of the history. The interface acquires amphifunctional behavior provided certain conditions related to the solid substrate are satisfied. These conditions are explicitly outlined below.

**2.2. Nature of the Systems under Modeling.** Only one of the charging processes directly depends on pH and indirectly depends on the applied potential. The protolytic sites are formed by the localized amphoteric groups ( $-\text{MOH}$ ). The second type of charging is of an electronic nature, the electrons being withdrawn (or supplied) from (to) the conducting surface by an external source. This process is only indirectly dependent on pH. Therefore, for an interface to behave amphifunctionally, the solid side should either consist of (i) a metallic conductor or semiconductor partially covered with a layer of binding sites, e.g., an oxidized metal<sup>19</sup> or an oxidized semiconductor<sup>33,34</sup> (type 1), or (ii) a conductive or semiconductive phase with intrinsic surface ion binding sites, e.g., an oxide with

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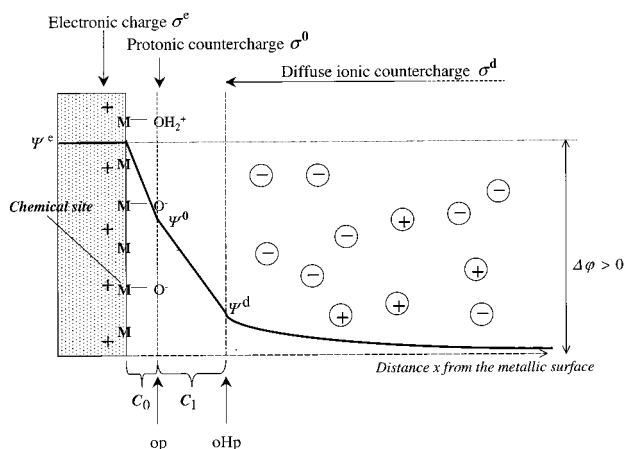
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**Figure 1.** Schematic representation of the DL model used to describe an amphifunctional interface between a partially oxidized metal and an aqueous electrolyte. The situation is depicted for an external potential  $\Delta\varphi > 0$ .

metallic conductivity or a semiconductive oxide<sup>35</sup> (type 2). In the frame of this paper and for the sake of illustration, the amphifunctionality potential/pH will be accounted for on the basis of a model describing the simplest situation where the amphifunctional analysis is not becoming more complex because of the occurrence of other phenomena made explicit later. Our model can be extended by taking into account the equations accounting for these phenomena.

### 2.3. DL Model for an Amphifunctional Interface.

Figure 1 depicts a schematic representation of the structure of the DL at an amphifunctionally electrified interface between an oxidized metal and an electrolyte solution (type 1) in the case where no other ionic species than protons specifically interact with the amphifunctional surface. This latter situation will be explicitly reported in more detail subsequently<sup>36</sup> in connection with papers from the Russian school, which so far have been the first to point out the issue of a double mechanism of charging, albeit in the restricted context of specific adsorption of anions.<sup>37–41</sup> The total charge at the interface consists of the protonic charge ( $\sigma^0$ ) and the electronic charge ( $\sigma^e$ ), the latter supplied by the external electric source. Considering the oxidic groups as part of the substrate, in accordance with the GCS model,<sup>42–44</sup> the solution side of the DL is subdivided into two parts: (i) an inner part, the Stern layer, including the amphoteric sites and (ii) a diffuse layer extending from the plane of closest approach for indifferent ions (outer Helmholtz plane, oHp) into bulk solution. To avoid any confusion with the traditional meaning of the inner Helmholtz plane in the Grahame or triple layer model<sup>45</sup> accounting for the occurrence of specific

adsorption of ions on a relaxed oxide surface, here we shall call the plane where the oxidic groups reside the oxide plane (op).

A necessary, but still not sufficient, condition for amphifunctionality is the presence of a spatial separation between the bare surface of the conducting material and the op. For interfaces of type 1, the capacitance of the layer situated between  $\sigma^0$  and  $\sigma^e$  should be sufficiently high (thin layer of oxide) so that a significant fraction of the potential applied is operational at the solution side of the interface to allow for amphifunctionality. Thus, in that case, the amphifunctional character of the interface is defined by a submonolayer of oxide. For interfaces of type 2, one would rather speak of a metallic or semiconductive oxide layer. A further surface characteristic relevant for amphifunctionally electrified interfaces is the way in which the chemical sites are distributed over the surface. We shall assume the surface to be flat and homogeneous with the functional groups randomly distributed. Diffuse DL calculations on the basis of smeared-out charges are allowed if the potential profile is essentially independent of the position on the surface. This is the case for systems that obey

$$/\kappa \ll 1 \quad (5)$$

where  $/$  is the average separation between chemical sites and  $\kappa$  is the reciprocal screening Debye length defined by

$$\kappa = (2F^2 I / \epsilon_0 \epsilon_{rw} RT)^{1/2} \quad (6)$$

where  $\epsilon_0$  is the dielectric permittivity of vacuum,  $\epsilon_{rw}$  is the relative permittivity of water,  $I$  is the ionic strength of the solution,  $F$  is the Faraday constant,  $R$  is the gas constant, and  $T$  is the temperature. For  $/\kappa \geq 1$ , the relevance of an equipotential op, defined by the loci of the oxygen atoms, becomes disputable and so does the monodimensionality of the DL. We shall not consider this situation.

In the following, it will be assumed that no charge transfer phenomena take place in the range of potentials investigated and that only charging/discharging of the DL occurs. Consequently, neither formation nor disappearance of oxide sites is taken into account and the parameter  $N_s$  is supposed to remain constant. This assumption is reasonable for interfaces of type 2 since the coverage rate of oxide surface is relatively high and the range of potentials where the DL is studied narrow. Some authors have summarized measured values for the surface density of protolytic sites ( $N_s$ ) of surfaces densely covered by oxide groups and reported values between  $2 \times 10^{14}$  and  $9 \times 10^{14}$  sites  $\text{cm}^{-2}$ .<sup>46</sup> On the contrary, the lower number of oxidic sites found for interfaces of type 1<sup>19</sup> renders the assumption in that case more pragmatic than realistic. Indeed, one expects the surface oxidation and, hence, the oxide coverage to be in that case very sensitive to pH and to the applied potential. The interface becomes therefore reversible and polarizable with a ratio depending on the two charging parameters. The function  $N_s(\text{pH}, \Delta\varphi)$ ,  $\Delta\varphi$  being the total potential difference applied across the metal/solution interphase, can be inferred from the experimental investigation of the electrochemical properties of the substrate immersed in the medium of given pH and salt concentration. We shall not discuss this complication.

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For amphifunctional substrates exhibiting semiconducting properties, a potential drop occurs in the bulk of the material so that there are potential and charge distributions within the space charge region. We shall neglect this solid diffuse layer in the following.

In usual DL analyses, it is assumed that ions remain fully charged during the adsorption process, that is, the full ionic charges are supposed to be localized at the op. In reality, however, because of covalency involved in O–H and M–O bonds,<sup>47</sup> the spatial electronic density distribution is altered, which effectively means that some charge separation is generated. This notion of partial charge transfer was first suggested by Lorentz<sup>48</sup> in the context of specifically adsorbed halide ions at the mercury surface and further developed by Vetter and Schultze.<sup>49</sup> As suggested by these authors, the partial charge transfer generally depends on the externally applied potential. As a first approach, we will here construct the modeling of the DL on the basis of full ionic charges of  $-\text{MO}^-$  and  $-\text{MOH}_2^+$ . Details of the real spatial distribution are then subsumed into the formal inner layer capacitance ( $C_0$ ), which models the decay of the potential between the bare surface of the substrate and the op and also accounts for the interfacial potential jump ( $\chi$ ). For the sake of simplicity, we will exclusively focus on an ideally flat surface for which the potential decay is one-dimensional and where  $C_0$  is estimated by

$$C_0 = \epsilon_0 \epsilon_r / d \quad (\text{F m}^{-2}) \quad (7)$$

Here  $\epsilon_r$  is the relative permittivity of the layer between the bare surface of the conducting substrate and the op, and  $d$  is the length of the chemical bond M–O. Equation 7 should be seen within the frame of the above modeling features.  $C_0$  is of the order  $5\text{--}10 \mu\text{F cm}^{-2}$ , roughly corresponding to a molecular condenser with a relative dielectric permittivity close to unity and a distance between the parallel planes delimiting the charge-free space of O (0.5 nm).

The total potential drop across the interface ( $\Delta\varphi = RT\Delta y/F$ ) is given by the relation

$$\Delta\varphi = \psi^e - \psi^\infty \quad (8)$$

where  $\psi^\infty$  is the potential of the bulk solution that is taken as the reference potential.  $\psi^e$  is the potential inside the bulk of the conducting phase. It is identical to the potential at the first layer of metallic atoms located in the close vicinity of the first layer of water molecules. Any deviations caused by orientation of water dipoles on the metal as well as on the solution side of the interface or induced by solid phase polarization of electronic or ionic origin are neglected. The contributions to the interfacial potentials ( $\chi$ ) are subsumed in  $C_0$  taken constant, and its probable dependencies on pH and potential are therefore not taken into account.

**2.4. Equations Describing the Potential and Charge Distributions at the Amphifunctional Interface.** It is assumed that the capacitance ( $C_0$ ) and the density of chemical sites ( $N_s$ ) do not vary with the position on the surface and that eq 5 is satisfied. Then, we may consider that the electric charge and potentials are smeared-out and write the equation of electroneutrality of the complete interphase as

$$\sigma^e + \sigma^0 + \sigma^d = 0 \quad (9)$$

where  $\sigma^d$  is the diffuse ionic charge as derived from the Gouy–Chapman theory for a 1:1 electrolyte<sup>42,43</sup>

$$\sigma^d = -(8I\epsilon_0\epsilon_r RT)^{1/2} \sinh(y^d/2) \quad (10)$$

with  $y^d$  the normalized dimensionless potential defined as

$$y^d = F\psi^d/RT \quad (11)$$

and  $\psi^d$  the potential at the oHp (generally approximated to the electrokinetic potential ( $\zeta$ ) at low ionic strength). For convenience, we shall use  $y^0$  for  $F\psi^0/RT$  and  $y^e$  for  $F\psi^e/RT$ , with  $\psi^0$  being the potential at the op.

The charge-free Stern layer acts as a molecular condenser represented by a capacitance ( $C_1$ ). Vorotyntsev<sup>50</sup> summarized results obtained by different authors concerning DL properties of “uniform” gold metal/electrolyte interfaces. For  $C_1$ , also called the Helmholtz capacitance, values between 15 and  $50 \mu\text{F cm}^{-2}$  are reported, depending on the surface roughness, the degree of polycrystallinity, and the crystallographic nature of the surface considered.  $C_1$  is generally obtained as a fit parameter of the so-called Parsons–Zobel plots derived from capacity measurements performed for different electrolyte concentrations at a given electrode charge density.<sup>51</sup> For an amphifunctional interface of type 1,  $C_1$  should therefore be written as a function of pH and the applied potential, these two variables determining  $\sigma^e$ . Taking into account such a dependence does not affect the general conclusions presented here, and consequently, as a first approximation,  $C_1$  will be considered as a constant parameter later. For interfaces of type 2,  $C_1$  is generally found to be substantially higher ( $100\text{--}140 \mu\text{F cm}^{-2}$ ).<sup>52</sup> In this latter case,  $C_1$  is commonly also supposed constant.

The activity coefficients of the bound ionic species and protons are assumed to be independent of  $\sigma^0$ .<sup>53</sup> Designating  $x$  as the distance counted from the bare surface of the metal, the concentration of unbound protons beyond the oHp noted  $c_{\text{H}^+}$  is, according to the Boltzmann law, given by

$$x > x_{\text{oHp}}: c_{\text{H}^+} = c_{\text{H}^+}^\infty \exp(-y(x)) \quad (12)$$

with  $c_{\text{H}^+}^\infty$  the concentration of protons in the bulk. Equation 12 is valid for the diffuse part of the DL where the work required to bring a proton from the bulk to the position  $x$  is of a purely electrostatic nature. To adapt eq 12 to the situation of chemisorption of protons at the op, one should realize that the driving force in such a case has two contributions: an electric component that brings the proton from the bulk to the oHp and a chemical component that binds the proton at the op. The chemical work is actually expressed by the corresponding constants ( $K_{a1}$  and  $K_{a2}$ ), which do not contain the electric contribution. Therefore, we can describe the chemisorption process via the two pertaining dissociation constants ( $K_{a1}$  and  $K_{a2}$ ) by considering eq 12 for  $y(x) = y^0$  as follows

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$$K_{a1} = [-\text{MOH}]/c_{\text{H}^+}^{\infty} \exp(-y^0)/[-\text{MOH}_2^+] \quad (13)$$

$$K_{a2} = [-\text{MO}^-]/c_{\text{H}^+}^{\infty} \exp(-y^0)/[-\text{MOH}] \quad (14)$$

The potentials  $\psi^e$ ,  $\psi^0$ , and  $\psi^d$  and the surface charges  $\sigma^e$  and  $\sigma^d$  are related via the capacitances<sup>54</sup> by

$$C_0 = d\sigma^e/d(\psi^e - \psi^0) \quad (15)$$

$$C_1 = -d\sigma^d/d(\psi^0 - \psi^d) \quad (16)$$

The complete set of equations (2, 3, 9, 10, and 13–16) for the potential and charge distributions at the amphifunctionally electrified interface can be rewritten in terms of one independent variable,  $\psi^d$ , for example. In the following, the notation  $X(Y)$  means “ $X$  function of  $Y$ ”, with  $X$  a charge or a potential and  $Y$  the parameter  $\psi^d$  or  $\Delta\varphi$ . With constant capacitances  $C_0$  and  $C_1$ , the transformed system of equations is

$$\psi^0(\psi^d) = \psi^d + ((8I_{\text{e}0}\epsilon_r RT)^{1/2}/C_1) \sinh(y^d/2) \quad (17)$$

$$\sigma^0(\psi^d) = \frac{(c_{\text{H}^+}^{\infty}/K_{a1}) \exp(-y^0(\psi^d)) - (K_{a2}/c_{\text{H}^+}^{\infty}) \exp(y^0(\psi^d))}{1 + (c_{\text{H}^+}^{\infty}/K_{a1}) \exp(-y^0(\psi^d)) + (K_{a2}/c_{\text{H}^+}^{\infty}) \exp(y^0(\psi^d))} eN_s \quad (18)$$

$$\sigma^d(\psi^d) = -C_1(\psi^0(\psi^d) - \psi^d) \quad (19)$$

$$\sigma^e(\psi^d, \Delta\varphi) = C_0(\Delta\varphi - \psi^0(\psi^d)) \quad (20)$$

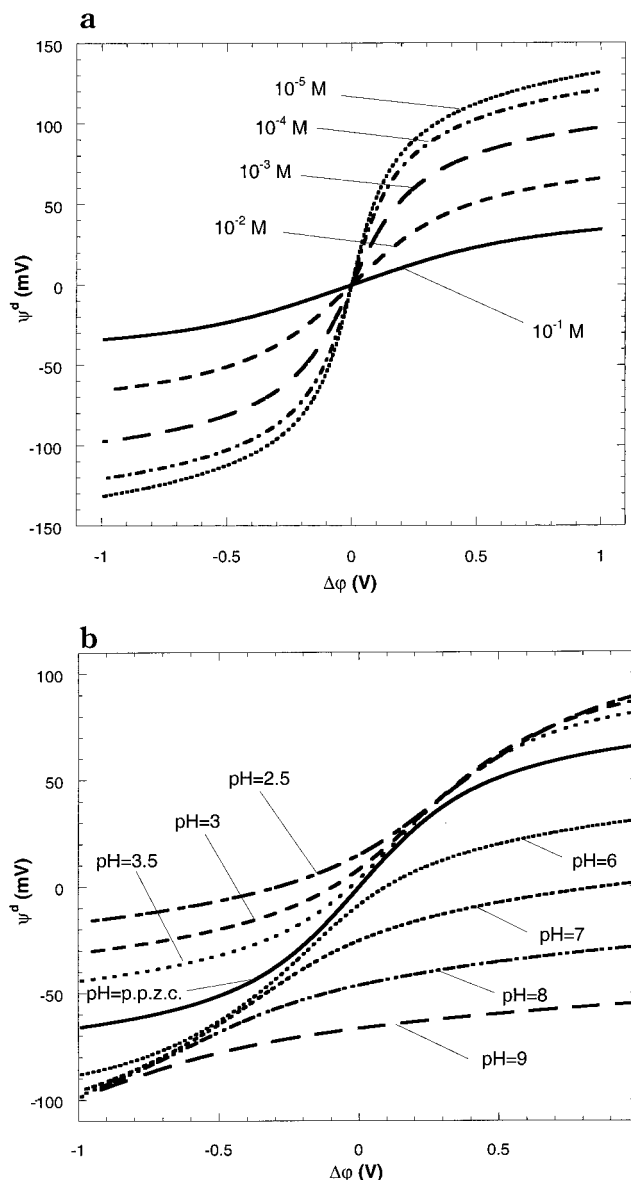
from which  $\psi^d$  is found as the solution of the following transcendental equation

$$\sigma^e(\psi^d, \Delta\varphi) + \sigma^0(\psi^d) + \sigma^d(\psi^d) = 0 \quad (21)$$

Once the relation  $\psi^d(\Delta\varphi)$  is known, all of the other parameters describing the DL can be computed as a function of  $\Delta\varphi$ .

At this stage of the discussion, it has to be stressed that the equations established above are written in forms suitable to analyze cases where  $\Delta\varphi$  is the independent electric parameter that can be fixed via an external potentiostatic source. The mathematical treatment of the galvanostatic situation would require rewriting of the equations describing the potential and charge distributions so as to obtain the relationship  $\psi^d(\sigma^e)$ .

For potentiostatic experiments, starting from the situation where the interface is relaxed (no external potential applied), one could conceive the influence of the applied potential on the DL formation in the following way: development of a potential difference across the interface, charging of the metallic phase by flow of electrons in the external circuit, accumulation of charge at the two sides of the interface, displacement of the adsorption equilibria, and redistribution of ions at the electrolyte side of the interface. In reality, these processes occur almost simultaneously. There is a functional relationship between the charges  $\sigma^e$ ,  $\sigma^0$ , and  $\sigma^d$  (or the potential difference across the interface) and the structure of the interfacial region. The difficulty is to unravel this functional relationship. In the following, we shall discuss the case of a DL resulting

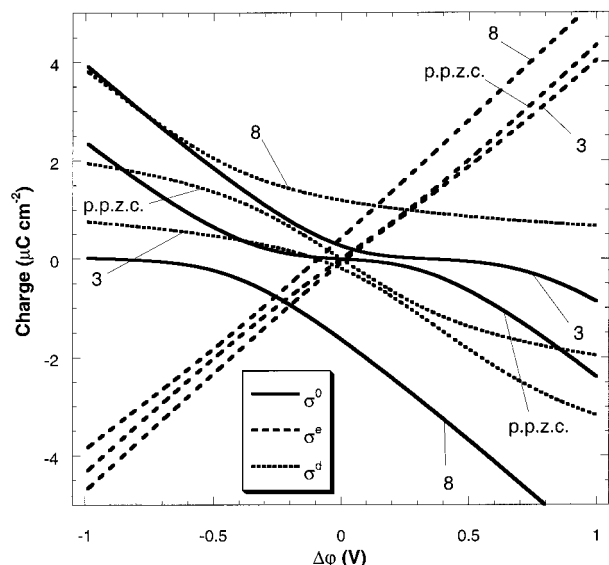


**Figure 2.** (a) DL potential as a function of the externally applied potential for various concentrations of indifferent electrolyte at a given pH = ppzc = 4.5. Parameters used for calculations:  $pK_{a1} = 1$ ,  $pK_{a2} = 8$ ,  $C_0 = 5 \mu\text{F cm}^{-2}$ ,  $C_1 = 30 \mu\text{F cm}^{-2}$ ,  $N_s = 3 \times 10^{14}$  sites  $\text{cm}^{-2}$ . (b) Dependence on the external applied potential for various pH values at a given electrolyte concentration  $10^{-2}$  M; ppzc = 4.5. Parameters used for calculations: same as in panel a.

from an externally applied potential difference, keeping in mind that the description of charging of the DL in separate steps is only relevant for explanatory purposes.

**2.5. Dependencies of the DL Properties on  $\Delta\varphi$  and pH.** Figure 2a represents  $\psi^d$  as a function of  $\Delta\varphi$  for different electrolyte concentrations and at pH = ppzc. All curves are symmetrical with respect to the origin. This is so because the equations derived in section 2.4 are invariant with respect to the signs of potentials and charges when replacing the ratio  $c_{\text{H}^+}^{\infty}/K_{a1}$  by  $K_{a2}/c_{\text{H}^+}^{\infty}$ , the latter condition resulting from our setting pH = ppzc. At a given  $\Delta\varphi$ ,  $\psi^d$  decreases with increasing ionic strength. This is a consequence of screening of the surface charge by counterions accumulating close to the surface. For a given concentration of electrolyte, starting from the situation at  $\psi^d = 0$ , an increase of  $\Delta\varphi$  renders the potentials  $\psi^d$  and  $\psi^0$  positive. By externally bringing the potential

(54) Lyklema J. *Fundamentals of Interface and Colloid Science*; Academic Press: London, 1995; Vol. 2, Chapter 3, p 3.61.



**Figure 3.** Dependence of the protolytic charge  $\sigma^0$  (—), the electronic charge  $\sigma^e$  (---), and the diffuse charge  $\sigma^d$  (···) on the external applied potential for three pH values at  $10^{-2}$  M; ppzc = 4.5. Parameters: same as in Figure 2.

of the metallic phase at positive values, one withdraws electrons from the conducting phase. The electronic charge therefore increases. The protolytic equilibria (a and b), which depend on  $\Delta\phi$  via the potential  $\psi^0$ , are displaced toward the formation of  $-\text{MO}^-$  sites, and consequently,  $\sigma^0$  decreases. In accordance with eq 10 and the dependence of  $\psi^d$  on  $\Delta\phi$ , the diffuse charge  $\sigma^d$  becomes negative. Throughout, the electroneutrality condition (eq 21) applies. A similar reasoning can be given for  $\Delta\phi < 0$ . Figures 2b and 3 show the dependencies of  $\psi^d$  and of the charges  $\sigma^d$ ,  $\sigma^0$ , and  $\sigma^e$  on the applied potential ( $\Delta\phi$ ) at given interfacial adsorption conditions, electrolyte concentration, and various values of pH. As expected, the curves for  $\text{pH} \neq \text{ppzc}$  are not symmetrical with respect to the origin. The more negative the difference ( $\text{pH} - \text{ppzc}$ ) is, the more the  $\psi^d(\Delta\phi)$  curves are shifted toward positive values. Indeed, by adding charge-determining  $\text{H}^+$  ions while maintaining a certain potential difference across the interface, the potential ( $\psi^0$ ) and the protonic charge ( $\sigma^0$ ) increase,  $\psi^d$  becomes more positive, and  $\sigma^d$  becomes more negative. At the given  $\Delta\phi$ , the total charge  $\sigma^d + \sigma^0$  is positive (if  $\Delta\phi < 0$ ) or negative (if  $\Delta\phi > 0$ ) since the inducing protonic charge ( $\sigma^0$ ) is always larger than the resulting diffuse charge ( $\sigma^d$ ). As a consequence, to compensate the charge  $\sigma^d + \sigma^0$ , the higher the pH of the solution is, the more positive the electronic charge ( $\sigma^e$ ) is rendered. The trends of the zero-charge and zero- $\psi^d$  points as a function of pH are analyzed in the next section.

**2.6. Relationships between  $\Delta\phi$  and pH at the iep and pzc Values.** For an amphifunctional interface, the situations encountered at the iep ( $\psi^d = 0$ ) and pzc values ( $\sigma^0 = 0$  and  $\sigma^e = 0$ ) are not described by one sole parameter such as the pH for a relaxed oxide/electrolyte interface<sup>46</sup> or the metallic potential for a mercury/electrolyte interface<sup>45,55</sup> but typically by the two charge-determining variables, viz.,  $\Delta\phi$  and pH.

**2.6.1. Situation at the iep.** Given the approximation  $\psi^d = \zeta$ , the condition of the iep, and the absence of specific adsorption of background electrolyte ions, it follows from eqs 18–21 that

$$\Delta\phi_{\text{iep}}(\text{pH}) = -\frac{eN_s}{C_0} \left( \frac{(c_{\text{H}^+}^\infty/K_{a_1}) - (K_{a_2}/c_{\text{H}^+}^\infty)}{1 + (c_{\text{H}^+}^\infty/K_{a_1}) + (K_{a_2}/c_{\text{H}^+}^\infty)} \right) \quad (22)$$

Figure 4 shows a plot of  $\Delta\phi_{\text{iep}}(\text{pH})$  for selected values of  $\text{p}K_{a_1}$  and  $\text{p}K_{a_2}$ . If the pH of the solution is brought to the value of the ppzc, the potential to apply across the interface to fulfill the condition  $\psi^d = 0$  is zero. For  $\text{pH} < \text{ppzc}$ ,  $\Delta\phi_{\text{iep}} < 0$ ; for  $\text{pH} > \text{ppzc}$ ,  $\Delta\phi_{\text{iep}} > 0$ . Let us define the pair ( $\Delta\phi = 0$ ,  $\text{pH} = \text{ppzc}$ ) as the pristine starting condition for further discussion. Starting from this condition (situation A in Figure 5), when charge-determining anions are added ( $\text{pH} > \text{ppzc}$ ),  $\sigma^0$  as well as  $\psi^d$  become negative and the resulting  $\sigma^e$  becomes positive, compensating the total countercharge  $\sigma^0 + \sigma^d$ . In this case, one can say that  $\sigma^e$  is protonically induced. This is situation B given in Figure 5, where the condition  $\psi^d = 0$  is no longer met. To reestablish the isoelectric situation,  $\Delta\phi$  has to be brought to positive values (situation C). At the newly reached iep, the charge at the metallic layer is more positive than in situation B since some electrons had to be withdrawn to increase  $\psi^e$ . To retain electroneutrality,  $\sigma^0$  is more negative than in situation B. Similar interpretations can be given for  $\text{pH} < \text{ppzc}$  and for the situations that consist in changing  $\Delta\phi$  while keeping the pH constant. For amphifunctional surfaces characterized by  $K_{a_1}$  and  $K_{a_2}$  values of the same order of magnitude (but still obeying  $\text{p}K_{a_1} < \text{p}K_{a_2}$ ), the pattern of the  $\Delta\phi_{\text{iep}}(\text{pH})$  plot is somewhat different from the one presented in Figure 4: the plateau region situated around the ppzc disappears and the potential  $\Delta\phi_{\text{iep}}$  changes drastically around the ppzc to reach the values  $-eN_s/C_0$  and  $eN_s/C_0$  for  $\text{pH} < \text{ppzc}$  and  $\text{pH} > \text{ppzc}$ , respectively. Further comments related to the DL at such surfaces will be given in section 2.7.1 when examining the conditions giving rise to asymptotic behavior of amphifunctional interfaces.

**2.6.2. Situation at the pzc.** The pzc<sub>1</sub> is defined as the condition where  $\sigma^e$  is zero. In this particular situation, resolution of the equations presented in section 2.5 allows us to obtain the dependence  $\Delta\phi_{\text{pzc}_1}(\text{pH})$ . On the basis of the reasoning used in the previous section, the trend of the curve  $\Delta\phi_{\text{pzc}_1}(\text{pH})$  (Figure 4) can be qualitatively explained. For  $\text{pH} = \text{ppzc}$ , the situations at the iep and pzc<sub>1</sub> are similar. These correspond to the pristine condition. Situation D in Figure 5 illustrates that because of the adsorption of  $\text{H}^+$  the dependence of pzc<sub>1</sub> on pH is opposite to that of the iep. Such a difference of behavior between pzc and iep is also encountered for relaxed oxide/electrolyte interfaces in the presence of specific adsorption.<sup>56</sup> In the terminology used by electrochemists,  $\Delta\phi_{\text{pzc}_1}$  is also called the “open-circuit potential”. When the conducting substrate exhibits a substantial surface oxidation ( $N_s > 10^{14} \text{ cm}^{-2}$ ),  $\Delta\phi_{\text{pzc}_1}$  tends to a Nernstian behavior with pH. The bulk properties of the material are then more oxidic than metallic, and consequently, the coupling pH/external potential is lost (see section 2.7). Most of the potential applied to the substrate decays in the insulating oxide layer so that only a small fraction of this potential remains at the op. One consequence of such a behavior is the independence of the parameter  $\text{pH}_{\text{iep}}$  on  $\Delta\phi$ . This was observed for a number of “metals” such as Pt.<sup>57,58</sup> On the contrary, metals such as gold, for which  $N_s$  is experimentally found to be lower, show a coupling pH/external

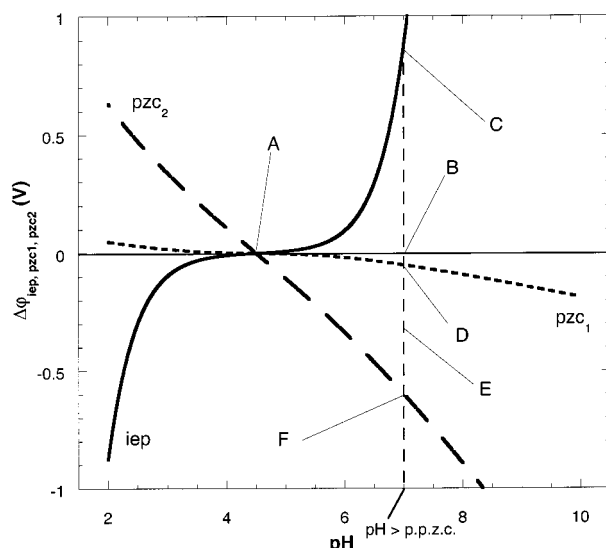
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(57) Gileadi, E.; Argade, S. D.; Bockris J. O'M. *J. Phys. Chem.* **1966**, *70*, 2044.

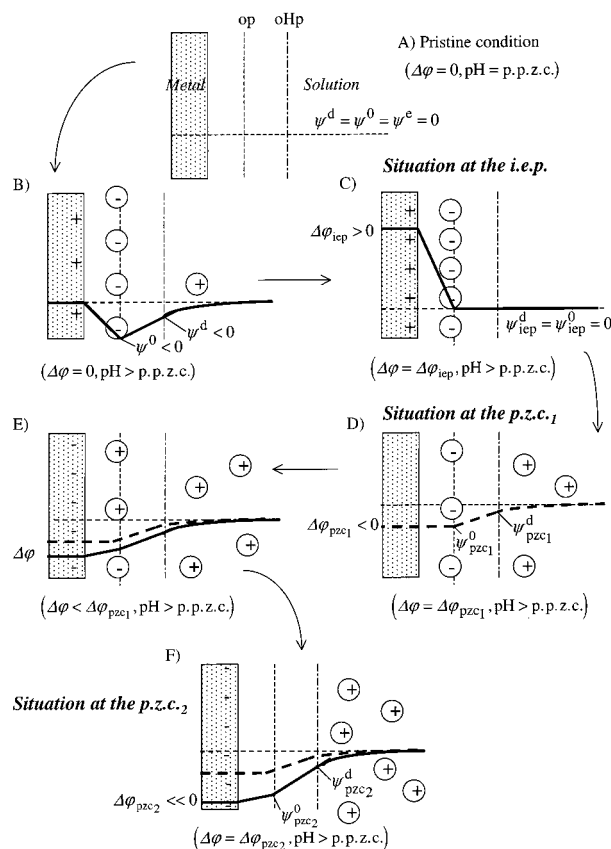
(58) Kallay, N.; Torbic, Z.; Golic, M.; Matijevic, E. *J. Phys. Chem.* **1991**, *95*, 7028.

(55) Baradas, R. G.; Conway, B. E. *Electrochim. Acta* **1961**, *5*, 349.





**Figure 4.** Plot of the potential necessary to apply across the interface to reach the iep, pzc<sub>1</sub>, and pzc<sub>2</sub> as a function of pH at 10<sup>-2</sup> M; ppzc = 4.5. Model parameters: same as in Figure 2. The points A–F refer to the schemes presented in Figure 5.



**Figure 5.** Sketches representing the potential and charge distributions at the iep, pzc<sub>1</sub>, and pzc<sub>2</sub> configurations. The potential profile drawn with a dashed line represents the pzc<sub>1</sub> situation.

potential, as manifest in a nonlinear behavior of  $\Delta\varphi_{pzc_1}$  (pH) and in a dependence  $\psi^d(\Delta\varphi, \text{pH})$ .<sup>19</sup>

**2.6.3. Situation at the pzc<sub>2</sub>.** The relationship  $\Delta\varphi_{pzc_2}(\text{pH})$  corresponding to pzc<sub>2</sub> is given by resolution of the equations describing the potential and charge distributions with  $\sigma^0 = 0$ . As expected, the curve  $\Delta\varphi_{pzc_2}(\text{pH})$  (Figure 4) has a common intersection point with  $\Delta\varphi_{pzc_1}(\text{pH})$  and  $\Delta\varphi_{iep}(\text{pH})$  for pH = ppzc (pristine condition). The trend of the curve  $\Delta\varphi_{pzc_2}(\text{pH})$  is similar to that for  $\Delta\varphi_{pzc_1}(\text{pH})$ . At a given pH,

the inequality  $|\Delta\varphi_{pzc_2}| \geq |\Delta\varphi_{pzc_1}|$  always applies. Indeed, starting from scheme D in Figure 5 and representing the situation occurring at the pzc<sub>1</sub> for pH > ppzc, it turns out that pzc<sub>2</sub> can only be reached by decreasing  $\Delta\varphi_{pzc_1}$ . This requires a decrease of  $\sigma^e$ , which renders  $\psi^d$  more negative and  $\sigma^d$  more positive. In response to the change of  $\sigma^e$ , the countercharge located at the op (protonic charge  $\sigma^0$ ) becomes more positive, as can be seen in situation E. At some point, the metallic potential  $\psi^e$  is such that  $\sigma^0 = 0$ : at that potential, the condition defining the pzc<sub>2</sub> is fulfilled (situation F). Similar reasoning can be given for pH < ppzc. The trend of the relationship  $\Delta\varphi_{pzc_2}(\text{pH})$  predicted by the model is experimentally confirmed in ref 59 for the IrO<sub>x</sub>/Ti/electrolyte interface.

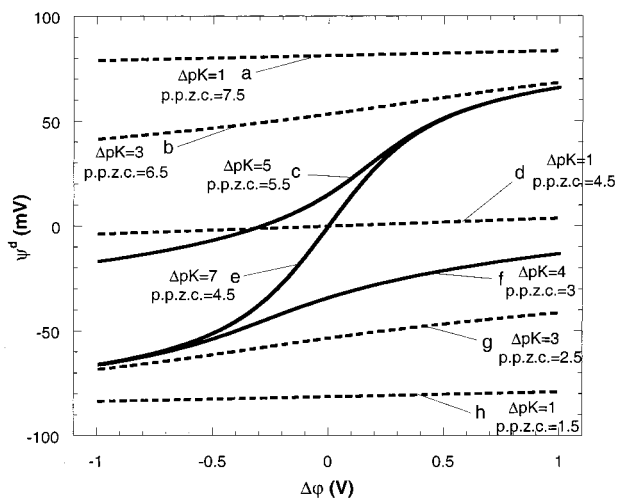
**2.7. Limiting Behavior of the Amphifunctionally Electrified DL: Loss of the Amphifunctional Character.** For conducting substrates fully covered by a layer of a nonconducting oxide, the thicker the layer is, the more  $\Delta\varphi$  will be dominated by the potential drop across the oxide layer. In the limit, the potential at the op is no longer affected by  $\Delta\varphi$  and the coupling between the electronic-charging and the ionic-charging mechanisms is lost.<sup>60</sup> This situation is generated for  $C_0 \rightarrow 0$ . For a purely metallic conductor, which constitutes the other known limit of the amphifunctional model ( $C_0 \rightarrow \infty$ ), the electronic surface charge, controlled by an external source, prevails over any ionic charge-determining processes as long as no depolarizers are present. The purpose of this section is to examine these two limiting conditions where the surface is basically amphifunctional (section 2.2) but approaches monofunctionality.

**2.7.1. Influence of the Acidic/Basic Character of the Surface on the Dependence  $\psi^d(\Delta\varphi, \text{pH})$ .** The surface has a relatively strong potential-buffering propensity when the two pK values defining the proton binding reactions are close together. This can be inferred from the influence of the pK values on the shape of the titration curves  $\sigma^0(\text{pH}, \Delta\varphi)$ . In the case of an amphifunctional interface, titration of the protolytic surface groups can be performed in two ways. One may vary the pH of the solution while maintaining a constant  $\Delta\varphi$ . This option constitutes the pendant of the titration curve  $\sigma^0(\text{pH})$  obtained for the relaxed case. It is also possible to keep the pH constant while varying  $\Delta\varphi$ . We will consider this latter situation for further reasoning. For a chosen set of two different pK values, the computed  $\sigma^0(\Delta\varphi)$  plots exhibit two waves corresponding to the successive titrations of the  $-\text{MOH}_2^+$  and  $-\text{MOH}$  surface species at  $\Delta\varphi < \Delta\varphi_{pzc_2}$  and  $\Delta\varphi > \Delta\varphi_{pzc_2}$ , respectively. The range of the external potential corresponding to the plateau situated between these two waves is the more extended when the difference ( $\Delta\text{pK} = \text{pK}_{a_2} - \text{pK}_{a_1}$ ) is larger. In the plateau regime,  $\sigma^0$  is practically insensitive to variations of the external potential. Then, the countercharge required to compensate the potential-induced  $\sigma^e$  is mainly located in the diffuse layer. In this plateau region,  $\psi^d$  (or  $\sigma^d$ ) is mainly affected by  $\Delta\varphi$ . In other words, the DL potential is badly buffered. Outside the plateau region, the large variations of  $\sigma^0$  indicate that a substantial fraction of the countercharge is situated at the op. Then, variation of  $\Delta\varphi$  generates only moderate change of  $\psi^d$  (or  $\sigma^d$ ): the DL potential is buffered. Therefore, for the case where  $\Delta\text{pK}$  is low and within the situation where the protonic charge is not saturated (see next section), the protolytic surface groups play the role of potential buffer: the pH at the op is practically constant

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(60) Ghowsi, K.; Naghshineh, S.; Houlne, M. P. *Russ. J. Electrochem.* **1995**, 31 (12), 1259.





**Figure 6.** Dependence of the DL potential on  $\Delta\phi$  at given pH = 4.5 and salt concentration ( $10^{-2}$  M) for surfaces characterized by different ppzc. Illustration of monofunctional behavior (dashed lines) of the interface of which the DL, under certain conditions ( $pK_{a1}$ ,  $pK_{a2}$ ), is only governed by the ionic-charging process. The plain lines refer to an amphifunctional behavior of the DL.  $C_0 = 5 \mu\text{F cm}^{-2}$ ,  $C_1 = 30 \mu\text{F cm}^{-2}$ ,  $N_s = 3 \times 10^{14}$  sites  $\text{cm}^{-2}$ . (a)  $pK_{a1} = 7$ ,  $pK_{a2} = 8$ . (b)  $pK_{a1} = 5$ ,  $pK_{a2} = 8$ . (c)  $pK_{a1} = 3$ ,  $pK_{a2} = 8$ . (d)  $pK_{a1} = 5$ ,  $pK_{a2} = 5$ . (e)  $pK_{a1} = 1$ ,  $pK_{a2} = 8$ . (f)  $pK_{a1} = 1$ ,  $pK_{a2} = 5$ . (g)  $pK_{a1} = 1$ ,  $pK_{a2} = 4$ . (h)  $pK_{a1} = 1$ ,  $pK_{a2} = 2$ .

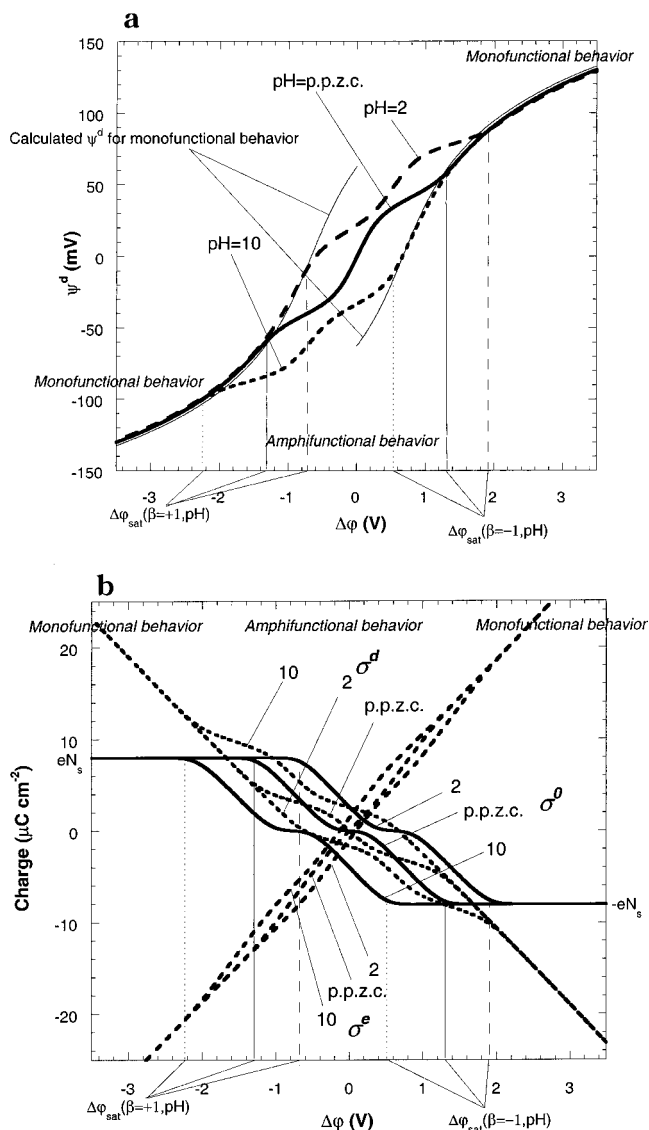
and independent of the potential applied. The S shape of the curves  $\psi^d(\Delta\phi)$ , which is characteristic of amphifunctional behavior (Figure 2b), then tends to a horizontal line, which by changing the pH (or ppzc) at constant ppzc (pH) is shifted as explained in section 2.5 (Figure 6). For these cases where the interface loses its amphifunctional character, the absolute value of the potential-induced charge ( $\sigma^e$ ) is practically equal to the induced protonic charge ( $\sigma^0$ ). One may speak of image-inducing and/or induced charges since

$$d\sigma^e/d\Delta\phi = -d\sigma^0/d\Delta\phi \approx C_0 \quad (23)$$

**2.7.2. Relationship  $\psi^d(\Delta\phi, \text{pH})$  at Saturated Surface Protonic Charge.**  $\sigma^0$  cannot exceed the saturation values  $\sigma_{\text{sat}}^0 = \pm eN_s$  whatever the conditions ( $\Delta\phi$ , pH). Saturation of  $\sigma^0$  can occur (i) at a given pH, when  $|\Delta\phi| \gg |\Delta\phi_{\text{ppzc}}|$  and (ii) at a given potential  $\Delta\phi$ , when  $\text{pH} \gg \text{pH}_{\text{ppzc}}$  or  $\text{pH} \ll \text{pH}_{\text{ppzc}}$ . Let us, for example, examine situation (i).

DL parameters become independent of pH at extreme  $\Delta\phi$ . This is illustrated by Figure 7a,b. In practice, for surfaces with relatively high  $N_s$ , the saturation can only be reached for  $\Delta\phi$  values that are so high that faradaic processes such as electrolysis of water and dissolution of the metal already depolarize the interface. However, for surfaces with relatively low  $N_s$ , saturation of the protonic charge occurs for potentials (or pH values) that do not generate per se such extreme electrochemical reactions and that therefore can be encountered experimentally. Then,  $\Delta\phi$  remains the only charge-determining parameter and for all practical purposes the interface behaves monofunctionally. The saturation values of  $\sigma^0$  can be written  $\sigma_{\text{sat}}^0 = \beta eN_s$ , with  $\beta = 1$  referring to  $\Delta\phi \ll \Delta\phi_{\text{ppzc}}$  (pH) and  $\beta = -1$  referring to  $\Delta\phi \gg \Delta\phi_{\text{ppzc}}$  (pH). Assuming that  $\psi_{\text{sat}}^0(\Delta\phi) \gg \psi_{\text{sat}}^d(\Delta\phi)$ , a simple explicit expression for  $\psi_{\text{sat}}^d(\Delta\phi)$  can be derived:

$$\psi_{\text{sat}}^d(\Delta\phi) \approx 2 \sinh^{-1} \left( \frac{\kappa C_1}{4FI} \frac{C_0 \Delta\phi + \beta eN_s}{C_0 + C_1} \right) \quad (24)$$



**Figure 7.** Representation of the potential regimes where the profile of the interface is determined by both types of charging processes (amphifunctional behavior) and where the DL is only controlled by the electric parameter (saturation regimes, monofunctional behavior). ppzc = 5.5,  $10^{-1}$  M. (a) DL potential as a function of  $\Delta\phi$ . (b) Charges as a function of  $\Delta\phi$  (same symbols as for Figure 3). Model parameters:  $pK_{a1} = 3$ ,  $pK_{a2} = 8$ ,  $C_0 = 12 \mu\text{F cm}^{-2}$ ,  $C_1 = 30 \mu\text{F cm}^{-2}$ ,  $N_s = 5 \times 10^{13}$  sites  $\text{cm}^{-2}$ .

The curves corresponding to eq 24 ( $\beta = \pm 1$ ) are plotted in Figure 7a. For the types of surfaces described in section 2.7.1 and for  $\text{pH} > \text{ppzc}$  or  $\text{pH} < \text{ppzc}$ , the iep situation is reached within the saturation regime of the protonic charge. Equation 24 provides  $\Delta\phi_{\text{iep,sat}} = -\beta eN_s/C_0$ : this value is in accordance with eq 22. The potentials  $\Delta\phi_{\text{sat}}$  ( $\beta = \pm 1$ ) required to reach the saturations of the protonic charge are equal in absolute value only for  $\text{pH} = \text{ppzc}$  and do not depend on the ionic strength.

In the domains of charge saturation,  $\sigma_{\text{sat}}^e$  and  $\sigma_{\text{sat}}^d$  vary linearly with  $\Delta\phi$  (see Figure 7b). One can show that

$$d\sigma_{\text{sat}}^e/d\Delta\phi = -d\sigma_{\text{sat}}^d/d\Delta\phi \approx C_0 C_1 / (C_0 + C_1) \quad (25)$$

In parallel to the situation reported in section 2.7.1 (eq 23), one then may use for  $\sigma_{\text{sat}}^e$  and  $\sigma_{\text{sat}}^d$  the terms image-induced and/or inducing charges.

### 3. Conclusions

A model is proposed for a quantitative description of the DL at interfaces of which the electric properties are governed by the coupling between ionic-charging and electronic-charging mechanisms. The dependencies of the DL properties on the electric and chemical state variables (externally applied potential, pH, and salt concentration) are analyzed. Particular attention is paid to situations occurring at the iep and pzc. Under certain limiting experimental potential/pH conditions, the coupling between the two charging processes is lost. In one of these limits, the electrostatic interactions resulting from the externally applied potential outweigh the ionic-charging function. On the other hand, the latter mechanism becomes predominant when the amphifunctional surface contains protolytic surface groups that bind protons and release protons in not too different pH (and potential) ranges. From the model presented in this paper, the DL profiles at a polarized metal electrode and at relaxed oxide/electrolyte interfaces are derived as limiting cases.

The theoretical formalism described in this paper successfully interprets AFM data on the DL at a gold/solution interface examined at various externally applied potentials and various pH values.<sup>19</sup> Furthermore, it allows interpretation of data relating to the dependencies on pH and potential of pzc of metals and oxide surfaces, respectively. A paper currently in preparation<sup>36</sup> focuses on the situation of an amphifunctional interface that specifically interacts with electrolyte ions or polyions.

### Glossary of Symbols

$l$	Average separation between the chemical sites
$C_0$	Capacitance of the layer between the bare surface of the metal and the op
$C_1$	Capacitance of the Stern layer (between the op and the oHp)
$C_{H^+}^\infty$	Concentration of protons in the bulk solution
$C_{H^+}$	Concentration of protons in the diffuse DL
$\beta$	Constant equal to $\pm 1$
$\epsilon_0$	Dielectric permittivity of vacuum
$\sigma^d$	Diffuse charge density
$x$	Distance counted from the bare surface of the metal
$\zeta$	Electrokinetic potential
$\sigma^e$	Electronic charge density
$e$	Elementary charge
$F$	Faraday
$R$	Gas constant

$\chi$	Interfacial potential jump
$I$	Ionic strength
$d$	Length of the chemical bond M–O
$pK_{a_1}$	Logarithm of the first dissociation constant $K_{a_1}$
$pK_{a_2}$	Logarithm of the second dissociation constant $K_{a_2}$
$y^d$	Normalized oHp potential
$y^0$	Normalized op potential
$\Delta y$	Normalized potential difference
$y^e$	Normalized potential of the metallic phase
$\psi^d$	Potential at the oHp
$\psi^0$	Potential at the op
$\Delta\varphi$	Potential difference between the bulk solid substrate and the bulk solution
$\psi^e$	Potential in the bulk metallic phase
$\psi^\infty$	Potential of the bulk solution taken as a reference
$\sigma^0$	Protonic charge density
$\epsilon_{r_1}$	Relative permittivity of the layer modeled by $C_0$
$\epsilon_{r_w}$	Relative permittivity of water
$\kappa$	Screening Debye parameter
$\gamma$	Surface tension
$T$	Temperature
$N_s$	Total number of surface oxidic sites

### Abbreviations

iep	Isoelectric point
pzc	Point of zero charge
pzp	Point of zero potential
ppzc	Pristine point of zero charge

### Subscripts

sat	Pertaining to the regimes where the saturation of $\sigma^0$ is reached
iep	Pertaining to the situation $\psi^d = 0$
pzc <sub>1</sub>	Pertaining to the situation $\sigma^e = 0$
pzc <sub>2</sub>	Pertaining to the situation $\sigma^0 = 0$

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