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New Insights into Electrosorption on Oxides. Application to Environmental Problems and the Photolysis of Water*

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The paper describes the general features of the interfacial chemistry of oxides, the model systems for a wide variety of colloids. Their importance is in their widespread occurence in nature, abundant application in industry, but even more for their intriguing double layer properties. The basic issue is that by proper interpretation of the classical double layer measurements insight may be obtained into phenomena of specific electrosorption of ions, at conditions which are below the detectability of analytical techniques.

INTRODUCTION

Over the past decades many systematic studies have been made of the double layer properties of colloids. Originally, such investigations have been motivated by the wish to improve the description of the electric repulsion between particles. The techniques used for this purpose are simple. Electrokinetics, analytical methods and direct determination of the surface charge σ_0 belong to them.

When in the earlier fifties systematic double layer studies on disperse systems started, excellent data for the mercury-solution interface were already available. Colloidally dispersed systems are not so well-defined as mercury, therefore the precision and reproducibility of the data on the former group were not so good as those for the latter. Typically, on cercury σ_0 can be measured with a precision of ca. 0.01 μC cm^{-2} whereas on silver iodide this is rather 0.1 μC cm^{-2}. However, this drawback is to a large extent compensated by three main advantages.

(1) In disperse systems, the interfacial area is often so high that adsorbed amounts can be analytically determined from depletion of the solution. For mercury drops, where the area is usually less than one cm^2 this is, as a rule, impossible.

(2) The possibility of doing on the same sample both surface charge- and electrokinetic measurements allows one to obtain additional, and sometimes

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essential information. With mercury this is very difficult, so that all interpretations tend to be based on capacitance curves only.

(3) The practical relevance of dispersions as such has stimulated the preparation of better defined systems and the improvement of the techniques.

The result is that at present the analysis of double layers in disperse systems has attained some sophistication and that even a number of new double layer features have been discovered. In the present paper some new developments in the domain of the electrical double layer on oxides will be discussed. The present study may be compared with a previous one[1], published 15 years ago in the same journal, to judge the progress that since then has been made.

SOME BASIC PRINCIPLES

In view of the applications, this paper devotes special attention to the detection and analysis od *specific adsorption of ions,* that is adsorption whereby the free energy contains a »chemical« term besides the Coulombic energy ($zF\psi(x)$ per mole where z is the valency of the ion, F, the Faraday constant and $\psi(x)$ the electric potential at the place x where the ion adsorbs). By »chemical« any type of interaction is understood that is not part of $zF\psi(x)$, even if it has basically an electric origin.

Ions for which the adsorption free energy is purely Coulombic are called *»indifferent«.* Such ions are attracted (=positively adsorbed or simply »adsorbed«) by a surface of opposite sign and repelled (=negatively adsorbed) by surfaces of like sign. One could also say that indifferent ions behave passively in that they comply with the requirements of the double layer potentials. Specifically adsorbing ions are, in this terminology, »active« because they can under some conditions adsorb against a repulsive electric potential.

The third category of ions is that of *surface ions,* that are ions having such an extremely high chemical affinity for the surface that after adsorption they may be considered to be part of this surface. The difference between surface ions and specifically adsorbing ions is quantitative rather than qualitative and may be compared with the difference between chemisorbed and physically adsorbed molecules at solid-gas interfaces. In the present paper no intermediate cases will be discussed where there is some doubt about their classification. Surface ions are also known as *potential-determining* ions. There is no objection against using this term in the qualitative sense that such ions are responsible for the creation of a potential on the particle surface, but the quantitative implication that this potential obeys Nernst's law is not a prerequisite.

For oxides, to which we shall henceforth restrict ourselves, it is obvious that protons can become surface ions because they can bind with a surface hydroxyl, say $\equiv$ROH through

$$\equiv \mathrm{ROH} + \mathrm{H}^+ \rightleftarrows \equiv \mathrm{ROH}_2^+ \tag{1}$$

A proton can also be withdrawn to render a surface site negative:

$$\equiv \mathrm{ROH} + \mathrm{OH}^- \rightleftarrows \mathrm{RO}^- + \mathrm{H}_2\mathrm{O} \tag{2}$$

Molecularly speaking, H^+ is the only surface ion: OH^- ions do not adsorb as such. Operationally however, the situation is different. The surface charge

$$\sigma_o = F\,(\Gamma_{ROH_2^+} - \Gamma_{RO^-}) \tag{3}$$

where Γ is the surface concentration of the species named, is usually determined by acid-base titrations. One can from, say, an increase in pH never decide if it is due to uptake of H^+ or release of OH^- from the surface. In other words, only the difference between $\Gamma_{ROH_2^+}$ and Γ_{RO^-} is measurable, not the individual values. Therefore, operationally H^+ and OH^- act both as surface ions and the operational (= thermodynamic) definition of σ_o reads

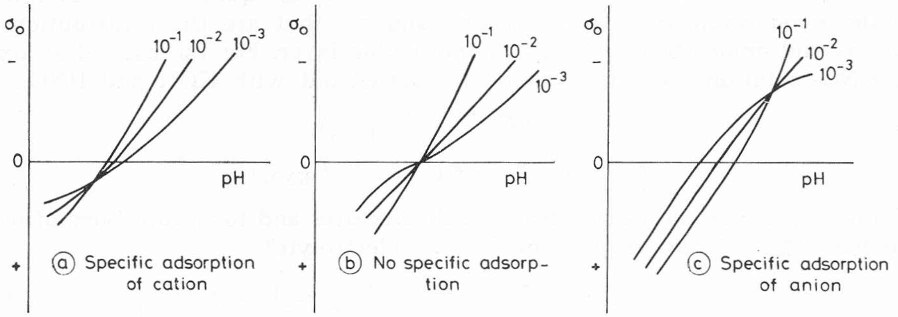
$$\sigma_o = F\,(\Gamma_{H^+} - \Gamma_{OH^-}) = F\,(\Gamma_{HNO_3} - \Gamma_{KOH}) \tag{4}$$

The latter of this pair of equations is preferred by the present author because it expresses the electroneutrality of double layers as a whole. Definitions (3) and (4) are almost identical. The difference is that (4) is more general in that no assumption is made concerning the nature of the charge-bearing groups.

It follows also immediately from this argument that the point of zero charge (p.z.c.), that is the pH where $\Gamma_{ROH_2^+} = \Gamma_{RO^-}$ is not a thermodynamic quantity: some model assumption must be invoked to establish it.

ZERO POINTS AND EQUAL AFFINITY POINTS

By potentiometric acid-base titrations at different salt concentrations, it is possible to obtain for each oxide in each type of electrolyte a family of σ_o (pH) curves. Often, such curves exhibit a common intersection point (c.i.p.) called »point of zero salt effect« (p.z.s.e) by Sposito[2]. Until a few years ago, these intersection points were identified as points of zero charge, but now it is known that this is only justified if the electrolyte is indifferent. For electrolytes containing specifically adsorbing cations, the c.i.p. is located to the positive side of the p.z.c., becoming more positive for stronger specific adsorption. Similarly, for specific adsorption of anions the c.i.p. is more to the negative side of the p.z.c., the stronger the anion adsorbs specifically.[3,4] The picture looks therefore as in Figure 1.



(a) Specific adsorption of cation

(b) No specific adsorption

(c) Specific adsorption of anion

Figure 1. Schematic picture of the location of common intersection points in σ_o (pH) curves. Only in indifferent electrolyte (case (b)) is the p. z. c. invariant with the salt concentration and identical to the pristine point of zero charge (p. p. z. c.)

In indifferent electrolytes (KNO_3 for most oxides) the p.z.c. does not shift upon addition of salt. This p.z.c. is a property of the oxide only and characterizes its acidity/basicity. Following Bowden *et al.*[5], we dubbed it therefore

»pristine point of zero charge« (p.p.z.c.). If cations adsorb specifically, the formation of RO^- groups is favoured at the expense of ROH_2^+ groups and a higher acid concentration in the solution is needed to re-balance Γ_{RO^-} and $\Gamma_{ROH_2^+}$; in other words, the p.z.c. shifts towards lower pH. By similar reasoning, the p.z.c. shifts to higher pH if anions adsorb specifically.

In passing, it may be recalled that the trends in the *isoelectric point* (i.e.p.) are just the opposite. Electrokinetic techniques measure the charge within the slipping plane, that is σ_o plus the specifically adsorbed charge. Specific adsorption of cations renders the electrokinetically active particle more positive so that the pH should be raised to make it electrokinetically neutral again. Likewise, specific adsorption of anions leads to a reduction of the i.e.p. Only for indifferent electrolytes do the p.z.c. and i.e.p. coincide; this is a criterion for pristine conditions. The difference between p.z.c. and i.e.p. and the departure of the c.i.p. from the p.p.z.c. are both measures of the extent of specific adsorption.

It may be added that the three cases of Figure 1. are fairly representative, but not exclusive. In some systems no sharp p.z.s.e. is observed. For example, on haematite (α-Fe_2O_3), case (a) is observed in $Ca(NO_3)_2$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$,[4] case (b) in KNO_3[6] and case (c) in Na_2SO_4[6,7].* However, for RuO_2 in KCl there is no sharp c.i.p.[8]

A thermodynamic analysis of intersection points in general and of c.i.p.'s in particular has recently been given[9] in terms of so-called *Esin-Markov coefficients,* defined as

$$\beta = \left(\frac{\delta \mathrm{pH}}{\delta \ln a_{\pm}} \right)_{\sigma_o} \tag{5}$$

These coefficients measure the horizontal distance between σ_o (pH) curves at different salt activity $a_{\pm}$ In intersection points $\beta = 0$, and in common intersection points (as in Figure 1) the situation $\beta = 0$ is characteristic for a given oxide-salt sombination. Starting with the Gibbs equation, β can be related to the *ionic components of charge* σ_+ and σ_-, that are the contributions of cations and anions to the charge in the double layer. For the case of an oxide in KNO_3 solution, the titrations being carried out with KOH and HNO_3,

$$\sigma_+ = \sigma_{K^+} = F\,(\Gamma_{KOH} + \Gamma_{KNO_3}) \tag{6}$$

$$\sigma_- = \sigma_{NO_3^-} = -F\,(\Gamma_{HNO_3} + \Gamma_{KNO_3}) \tag{7}$$

Similar equations can be written for salt mixtures and for electrolytes of other valence types. Generally, for one ($z_+ : z_-$) electrolyte[9]

$$\beta = -\frac{1}{z_+} \quad \frac{z_+ + z_-}{z_+ z_-} \left(\frac{\delta \sigma_-}{\delta \sigma_o} \right)_{a\,\pm} = \frac{1}{z_-} + \frac{z_+ + z_-}{z_+ z_-} \left(\frac{\delta \sigma_+}{\delta \sigma_o} \right)_{a\,\pm} \tag{8^{a,b}}$$

For indifferent (1 : 1) electrolytes (Figure 1 (b)) at the c.i.p. = p.p.z.c., this leads to a familiar result: at that point

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* It must be noted that at the time this work was published the authors thought that the c.i.p. coincided with the p.z.c., hence the curves must be shifted along the σ_o-axis.

$$\left(\frac{\delta\sigma_-}{\delta\sigma_o}\right)_{a\,\pm} = \left(\frac{\delta\sigma_+}{\delta\sigma_o}\right)_{a\,\pm} = -\,1/2 \tag{9}$$

meaning that an infinitesimal change in σ_o is for 50% compensated by anions and for 50% by cations. This results also from Gouy-Chapman theory. Obviously, at the p.p.z.c. σ_o is zero and there is no countercharge, but if the surface is made slightly positive, half of this charge is compensated by adsorption of anions and the other half by *negative* adsorption of cations. Similarly, for a small change of σ_o in the negative direction this negative increment is equaly compensated by (positive) adsorption of cations and negative adsorption of anions. Such an equal compensation of σ_o is intuitively expected, since the c.i.p. is a symmetry point with respect to the adsorption of cations and anions. One could call such a point therefore also an »*equal compensation point*« or »*equal affinity point*«. For surface charges far outside the p.p.z.c. the compensation is no longer fifty-fifty, in fact if σ_o becomes very high positive, the countercharge is almost exclusively determined by (positive) adsorption of anions.

If the electrolyte is indifferent but, say, of the (2 : 1) type at the c.i.p.

$$\left(\frac{\delta\sigma_-}{\delta\sigma_o}\right)_{a\,\pm} = -\frac{1}{3} \qquad \left(\frac{\delta\sigma_+}{\delta\sigma_o}\right)_{a\,\pm} = -\frac{2}{3} \tag{10^{a,b}}$$

The difference with the previous case is due to the fact that at equal amount adsorbed a bivalent cation is twice as effective as a monovalent anion.

Let us now consider the situation of specific adsorption, taking $Ca(NO_3)_2$ on haematite as the example. This system leads to curves of type (a) in Figure 1. At the p.z.c. there is now no equal compensation because Ca^{2+} ions adsorb preferentially over NO_3^-. When the concentration of $Ca(NO_3)_2$ is increased, more Ca^{2+} ions adsorb and the shift to the left of the p.z.c. reflects this process. However, at the c.i.p. the two identities of (10) apply, meaning that at this positive surface charge an increment in σ_o is compensated by equal amounts of adsorbed Ca^{2+} and NO_3^-. The logical physical interpretation is that at the c.i.p. the electric potential in the double layer at the distance from the surface where the Ca^{2+} ions adsorb is just so high that the chemical affinity of Ca^{2+} ions for the surface is exactly balanced. By consequence, at this point there is no preference of Ca^{2+} above NO_3^- any more, so that one can again speak of an equal affinity point. The term »equal incremental compensation point« may also be used, but is a bit unwieldy.

With the above in mind, it is now easy to understand that the c.i.p. must be more positive for more strongly specifically adsorbing cations. Situation (c) of Figure 1 is entirely similar.

It can now also be understood why so often sharp c.i.p.'s are found; addition of electrolytes with equal affinity of the cation and anion for the surface does not lead to changes in σ_o. Such changes do occur, however, if complications occur, e. g. if there is a second electrolyte present at the interface (often unintentionally), gradual replacement may take place; then no sharp c.i.p. is found.

In the following sections some applications will be given.

THE ELECTRICAL DOUBLE LAYER ON HOMODISPERSE HAEMATITE SOLS

Homodisperse colloids attract increasing attention because of a multitude of applications, for example as model colloids, heterogeneous catalysts, and as basic materials for ceramics.

In our department, homodisperse haematite (α-Fe_2O_3) sols have recently been prepared in amounts that were sufficiently high to perform acid-base titrations.[10,11] Details of these titrations have been published elsewhere.[12] For the present purpose, we report here the analysis of the ionic components of charge, based on (8). As the electrolyte is KCl, $z_+ = z_- = 1$. Eq. (8) can be integrated to give

$$\sigma_+ = -\frac{\sigma_o}{2} + \frac{1}{2}\int_0^{\sigma_o} \beta d\sigma_o + \sigma_+ (\sigma_o = 0) \qquad (11a)$$

$$\sigma_- = -\frac{\sigma_o}{2} - \frac{1}{2}\int_0^{\sigma_o} \beta d\sigma_o + \sigma_- (\sigma_o = 0) \qquad (11b)$$

If at the p.z.c. the amounts adsorbed of K^+ and Cl^- are known, σ_+ and σ_- can be obtained over the entire pH-range. For KCl on haematite there is solid evidence that no specific adsorption occurs. One of the arguments is that the p.z.c. and the i.e.p. are nearly identical. Hence, for KCl $\sigma_+ (\sigma_o = 0) = \sigma_- (\sigma_o = 0) = 0$.

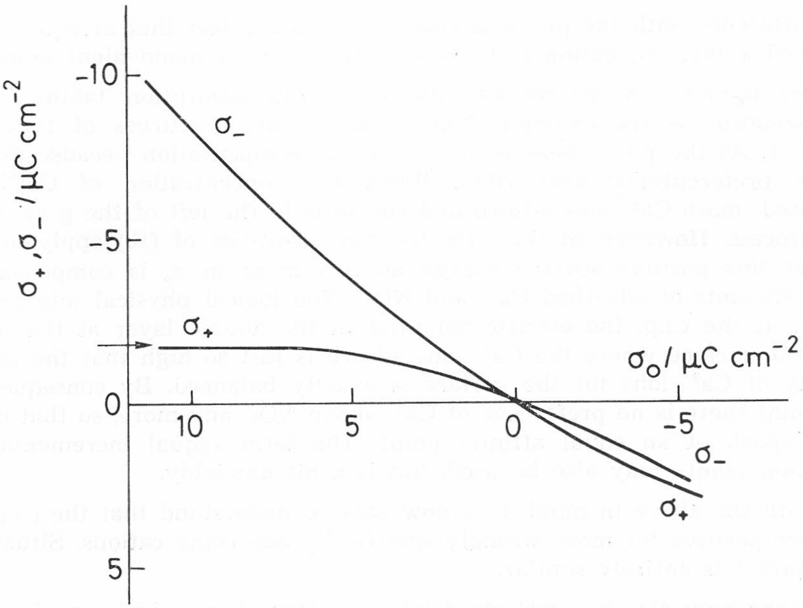


Figure 2. Electrical double layer on homodisperse haematite (α — Fe_2O_3). Ionic components of charge in 10^{-1} M KCl. The arrow indicates the plateau value of σ_+ according to diffuse double layer theory.

Figure 2 gives the result. In considering this diagram, it must be realized that first taking differences between curves and then integrating these differences calls heavily on the precision of the data. In this respect the data for

$\sigma_o > 0$ (left side of the p.z.c. in Figure 2) are more reliable and we shall discuss only this part.

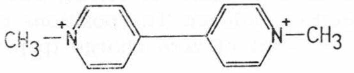
The first feature that can be noted is that for very low positive σ_o, $\sigma_+ = \sigma_- (= -\sigma_o/2)$, as predicted. When σ_o grows, σ_- grows also but σ_+ levels off. The reason is, that the concentration of anions near the surface can grow without too strong restrictions, whereas the concentration of expelled cations can never become lower than zero. In that case, the distribution is governed by diffuse double layer theory, because for ions that are absent there is no need to consider specific adsorption in the Stern-layer. According to this theory[13] for (1 — 1) electrolytes

$$\sigma_+ = \sqrt{\frac{\varepsilon\varepsilon_o\, cRT}{2\pi}}\left[1 - \exp.\left(\frac{-F\psi_d}{2RT}\right)\right] \tag{12}$$

where ε is the dielectric constant of the medium, $\varepsilon_o = 8.854 \times 10^{-12}$ CV^{-1} m^{-1}, ψ_d is the potential of the diffuse part of the double layer, and the other symbols have their usual meaning. For very positive surfaces $\sigma_+ \rightarrow (\varepsilon\varepsilon_o\, cRT/2\pi)^{1/2} = 1.86\ \mu$C cm^{-2} in 10^{-3} M solution, the value indicated in Figure 2 by an arrow. The agreement is gratifying and confirms the correctness of the absence of specific adsorption at the p.z.c.

ADSORPTION OF METHYLVIOLOGEN ON RuO_2

Methylviologen (MV^{2+}) has the following chemical structure



(13)

and for several reasons it is an interesting substance. The molecule can easily pick up an electron to become a fairly stable radical. Because of this, it acts as a »relay« in one of the procedures to photolyse water: (solar) photons are absorbed by some suitable dye, which transfers an electron to a MV^{2+} molecule. This substance, in turn transports the electron to the surface of a finely dispersed catalyst, e. g. colloidal Pt or RuO_2 which eventually catalyses the reduction of a H_2O molecule. Methylviologen is also used as a herbicide and then known as paraquat. The herbicide activity is probably due to the fact that MV^+ radicals are easily oxidised, whereby peroxides are formed that destroy plant tissues.

It goes without saying that adsorption of MV^{2+} is an important issue. For environmental problems it is relevant to know how strongly this herbicide accumulates in soils and how sensitive this accumulation is to salts, rainfall etc. In connection with the catalytic photolysis of water one of the key questions is by which mechanism adsorbed MV^+ radicals transfer their electron to the solid. Should the molecule adsorb very strongly or is a weak attachment enough? Or, in terms of the present study: is is the adsorption of methylviologen specific or not?

In order to solve this question we studied the double layer on RuO_2 in the presence of MV $(NO_3)_2$ and Figure 3, taken from a more detailed study to be published elsewhere,[14] shows one of the crucial results. It is observed that the curves pass through a common intersection point, slightly to the positive side of the p.p.z.c., indicating that MV^{2+} ions do adsorb specifically. It

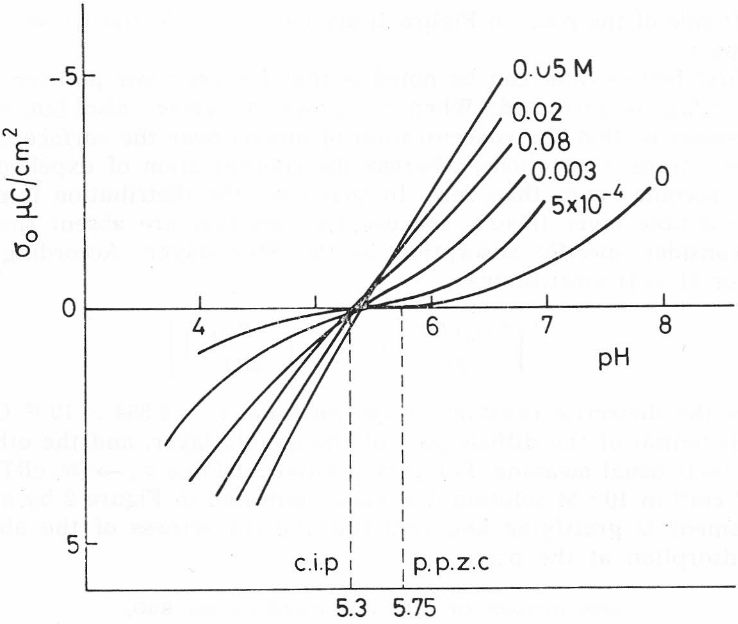


Figure 3. Electrical double layer on ruthenium dioxide (RuO_2). Surface charge in solutions containing small but variable amounts of KNO_3, due to the titration, and the indicated concentrations of methyl viologen The positions of the common intersection point (c. i. p.) and pristine point of zero charge (p. p. z. c.) are indicated.

is around this pH value that photolysis systems usually operate. However, the specific adsorption is not strong. It is, for example, less than that of Ca^{2+} ions on haematite. The specific adsorption energy of the radical MV^+ is probably not very different, because of the similarity with respect to the chemical structure. All of this suggests that the electron transfer between a MV^+ radical and a surface is a quick event, a »hit an run« rather than a chemisorptive exchange process with long residence times. Of course, the recharging of MV^+ to MV^{2+} helps to desorb it from positive surfaces. All of this illustrates how double layer studies can contribute to the understanding of colloidal catalysis mechanisms.

The rather weak specific adsorption of MV^{2+} under the given experimental conditions implies also that adsorbed MV^{2+} and MV^+ ions are fairly easily exchanged by other cations. This issue is not only relevant for the development of photolysis systems for solar energy conversion, in which usually several ionic admixtures are present, but also for agriculture. Here the question is, to which extent paraquat adsorbed in soils can be washed away by rain or exchanged against other cations. Experiments in our department by Fokkink and De Keizer showed that paraquat adsorbs very strongly on clay particles. Only that part of the paraquat that adsorbed on the oxide fraction after saturating much of the clay fraction in loess could be fairly easily exchanged against Na^+ ions.

ADSORPTION OF HEAVY METALS ON OXIDES

Binding of heavy metals to various oxides is not only of purely academic interest but has also environmental relevance. One aspect it the accumulation of poisonous heavy metals in the oxide fractions of soils. As in the example with paraquat, it is important to know how strongly these ions bind, how easily they are washed away or exchanged against other ions, Na^+ in particular. Again, the physical problem can be rephrased as »how strong is the specific binding (free) energy and what is the binding mechanism?.« Over the past decades this question has drawn considerable attention.

As far as σ_o(pH) curves are available (e. g. Ca^{2+}, Cd^{2+} and Pb^{2+} on haematite) invariably type (a) behaviour (Figure 1) is found, indicating specific adsorption. However, there is an interpretational problem in the case of adsorption of hydrolysing species. According to the operational definition of σ_o (Eq. (4)), this quantity does not only measure that part of OH^- ions that are used to deprotonate a surface $\equiv$ ROH group (2), but also the OH^- ions that are co-adsorbed with a cation. This problem makes the interpretation more difficult; one would like to have an additional piece of information to discriminate between the two different mechanisms of hydroxyl uptake. Similar questions can be asked about the sorption of H^+ ions.

Problems like the above are now under study in our Department by L.G.J. Fokkink. One promising approach to obtain useful additional information is to study the temperature dependence of the amount of cation adsorbed. In principle, such studies could lead to insight into the entropic and energetic factors that are responsible for the binding.[15] Figure 4 gives some results.

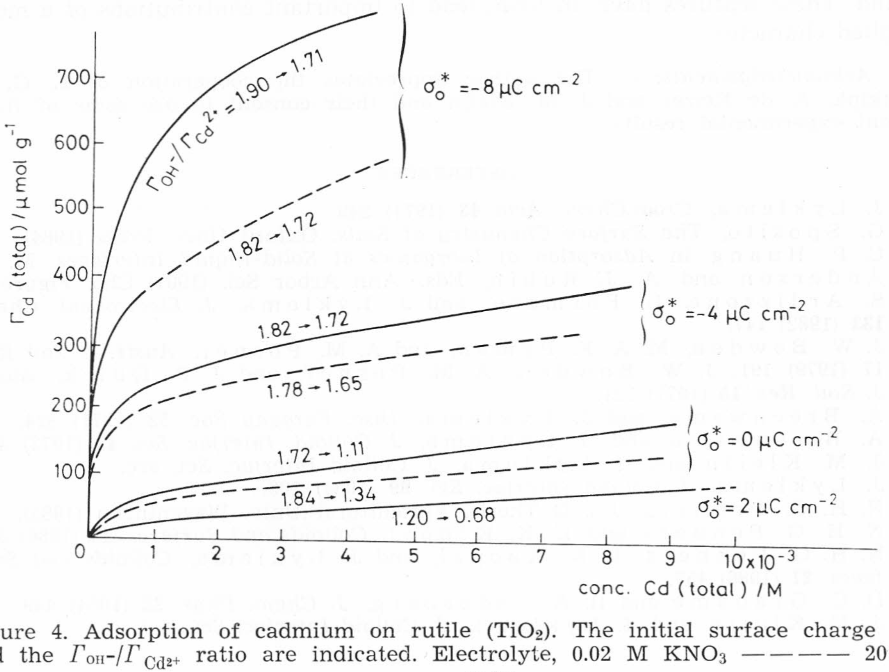


Figure 4. Adsorption of cadmium on rutile (TiO_2). The initial surface charge σ_o^* and the $\Gamma_{OH^-}/\Gamma_{Cd^{2+}}$ ratio are indicated. Electrolyte, 0.02 M KNO_3 – – – – 20 °C ——— 60 °C.

In this figure the initial surface charge σ_o^* is given, that is the surface charge before cadmium is adsorbed. Due to the adsorption σ_o becomes more negative but, as stated before, it is difficult to say by how much. As expected, the adsorption of cadmium increases if σ_o^* becomes more negative. The fact that cadmium adsorbs specifically can be inferred from the observation that even at positive σ_o^* adsorption takes place. An interesting feature is the increase in adsorption with temperature. On superficial inspection this suggests that the cadmium adsorption is endothermic, so that the process must be entropically driven, but this is an oversimplification. As will be set forth later,[16] co-adsorption of hydroxyls may not be ignored and this coadsorption plays a decisive role in the adsorption thermodynamics. In this connection it may be noted that at positive σ_o^*, where the pH is so low that Cd^{2+} ions do not hydrolyse, the temperature coefficient of the cadmium adsorption is zero. In the experiments of Figure 4, the pH of the solution was kept constant by adding KOH during the cadmium adsorption. From the amounts of KOH needed, the co-adsorption of hydroxyl ions Γ_{OH^-} could be computed and in Figure 4 the ratio $\Gamma_{OH^-}/\Gamma_{Cd^{2+}}$ is also indicated. This ratio decreases along the isotherms and increases with σ_o^*, that is: with increasing pH. If enough OH^- ions are available the ratio always approaches a value close to 5/3, irrespective of σ_o^*. Obviously, this observation sheds some light on the adsorption mechanism.

CONCLUSIONS

This paper is a progress report on the potentialities of basic double layer studies with oxides. It is shown, that over the past decades the sophistication of the experiments has so much improved that qualitatively new features are found. These features have, in turn, lead to important contributions of a more applied character.

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SAŽETAK

Novi pogledi na elektrosorpciju. Primjena na probleme u okolišu i na fotolizu vode

J. Lyklema

U radu se razmatraju mogućnosti koje pruža proučavanje dvosloja na površinama oksida, modelnih sustava za čitav niz različitih koloida. Važnost je oksida znatna, ne samo zbog njihove rasprostranjenosti u prirodi te široke primjene u industrijskim postupcima, već i zbog osnovnog interesa za svojstva njihova graničnog sloja. Pokazano je da se pravilnom interpretacijom mjerenja svojstava električkog dvosloja mogu dobiti podaci o specifičnoj elektrosorpciji iona, i to pri koncentraciji pri kojima druge analitičke metode zakazuju.

Prednosti proučavanja oksidnih sustava sastoje se u tome što velika specifična površina omogućuje analitičko određivanje smanjenja koncentracije adsorbata u otopini, zatim što se na istom sustavu mogu izvršiti mjerenja i površinske gustoće naboja i elektrokinetičkih svojstava, te što su zbog važnosti oksida razrađeni postupci za njihovu pripravu kao vrlo dobro definiranih materijala. U radu se redom razmatraju osnovni principi metodologije, problem nultočke površinskog naboja i točke jednakog afiniteta za elektrolite s ionima koji se specifično adsorbiraju, te posebno još i adsorpcija iona teških metala na oksidnim površinama. Primjena osnovnih principa metodologije istraživanja razrađena je na primjeru izračunavanja površinskog naboja homodisperznog hematita te za adsorpciju metilviologena na RuO_2.