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Conference Paper

The Electrical Double Layer on Oxides*

J. Lyklema

Laboratory for Physical and Colloid Chemistry, Wageningen, Netherlands

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The properties of the electrical double layer at the interface between oxides and aqueous electrolyte solutions have been studied on the basis of apparent surface charge — *p*H curves. It appears that all oxides studied so far can bear very high surface charges without giving rise to particularly high electrokinetic potentials. The trend is that this charge is the higher, the more porous is the surface layer. These results are discussed in terms of a quantitative theory, based on the concept that potential-determining as well as counter ions can penetrate into the solid, to an extent depending on the porosity of the surface for that ion. The theory and experiments are also applied to the glass-solution interface. The results seem to support the idea that glass-electrode potentials are diffusion potentials.

1. *Introduction*

There can be little doubt that the double layer at the Hg/solution interface is by far the most extensively studied. Several properties of this interface are particularly conducive to refined double layer work, notably the fact that mercury is a liquid, enabling studies with a continuously renewed interface, thus reducing the effect of adsorbable impurities to a minimum. Another advantage is that mercury electrodes are very polarizable: double layer studies can be made over a large range of applied potentials (E ~ 2000 mVolts). The basic experimental information consists of differential capacitance C and electrocapillary curves, both of which can be measured with high reproducibility and precision, at least in the presence of simple electrolytes.

As compared with the mercury system, solid metals are much more difficult to study. Although progress has been made in this field, the perfection obtained is considerably less than that on mercury.

Besides mercury and other metals, double layer studies can also be made on non-metals like silver iodide and insoluble oxides. The experimental techniques are as a rule quite different for these systems, and this is primarily a consequence of the reversible character of these interfaces. The electrical double layer is now due to adsorption of potential determining ions, whose surface excesses Γ can be measured. The potential across the interface is a consequence of this adsorption, hence the potential is a *derived* quantity, rather than an applied one, as with mercury.

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From a pure double layer point of view, the precision with which double layer parameters can be measured is much lower than for mercury due to causes such as adsorption of impurities, finite solubility, irreproducibility in the preparation of the interface and chemical reactions occurring at the interface. However, these drawbacks are partly offset by the circumstance that stable colloidal solutions (sols) of silver iodide and oxides can be made, enabling the measurement of flocculation values C_c and electrokinetic potentials ζ, quantities that are closely related to the charge distribution in the electrical double layer and thus furnish important auxiliary information. For example, the primary surface charge σ_0 data for silver iodide, are not sufficiently extensive to allow a computation of the charge in the Stern-layer, σ_m (which *is* possible for mercury) but as from experimental values of ζ and/or C_c the charge in the diffuse part of the double layer σ_d can be derived, σ_m can be estimated with fair accuracy by subtraction: $|\sigma_m| = |\sigma_0| - |\sigma_d|$.

Below, a discussion will be given of double layers on oxides using surface charge data in combination with information from the colloid chemical side. It will appear that all oxides studied so far have some characteristics in common.

2. *Charge and Potential for Oxide Double Layers*

H^+ and OH^- ions are *potential determining* for all oxides over a pH-range depending on the nature of the oxide (notably on its solubility). Taking silica as an example, a silanol group at the surface, represented schematically as $\equiv$ SiOH, can adsorb a proton at low *p*H to yield a positive surface:

$$\equiv SiOH + H^+ \leftrightarrows \equiv SiOH_2^+ \tag{1}$$

At higher *p*H the surface becomes negative through adsorption of a hydroxyl ion:

$$\equiv SiOH + OH^- \rightleftarrows \equiv SiO^- + H_2O \tag{2}$$

The adsorbed amounts of H^+ and OH^- can be determined analytically. More precisely, the amount of H^+ or OH^- taken up if the *p*H is changed can be determined so that (given the surface area) a *relative* surface charge

$$\sigma_0 \equiv F\,(\Gamma_{H^+} - \Gamma_{OH^-}) \tag{3}$$

can be determined. This relative surface charge can be made *absolute* if the *point of zero charge* (p. z. c.) is known, that is the pH at which $\sigma_0 = 0$. We shall denote it by *p*H°.

Several methods of determining *p*H° are available. The best approach is perhaps the one that is based upon the consideration that in the absence of specific adsorption (no preferential adsorption of non-potential determining ions on the uncharged surface) σ_0 is independent of c_{salt}. If short potentiometric titrations are made to determine the relative surface charge as a function of *p*H at various c_{salt} the curves intersect in the p. z. c. If there *is* specific adsorption *p*H° shifts with c_{salt}. This shift follows also from the titration method just mentioned. *p*H° becomes higher due to specific adsorption of anions and lower with specific adsorption of cations. Using this procedure for SiO_2, a value of *p*H° = 2 — 2.5 is found and for hematite ($\alpha - Fe_2O_3$) *p*H° = 8.5. These results have been corroborated by alternative methods of determination.

Two remarks must be made. In the first place: the p. z. c. is not necessarily identical with the *isoelectric point* (i. e. p.), which is the pH where electrophoretic mobility, streaming potential *etc.* are zero. The i. e. p. measures in the first approximation the potential of the diffuse part of the double layer ($\zeta \sim \psi_d$) and hence reflects only indirectly the situation at the surface. It is quite possible that σ_0 is high and negative, σ_m equally high and positive so that σ_d and ψ_d are zero and the particles are found at their i. e. p. without being at the p. z. c. An example is found for hematite where, due to specific adsorption of Ca^{2+}, the p. z. c. decreases with $[Ca^{2+}]$, whereas the i. e. p. increases[1]. In fact, many of the p. z. c. 's collected by Parks[2] are virtually i. e. p. 's and interpretation of them as real p. z. c. 's is not correct in general. Only if specific adsorption can definitely be excluded, i. e. p. and p. z. c. may be identified.

The second remark concerns the interpretation of p. z. c. 's. The low $p\mathrm{H}^\circ$ for silica indicates that SiO_2 is very »acid«, whereas $\alpha - Fe_2O_3$ is more »basic«. In fact, $p\mathrm{H}^\circ$ can be related to the equilibrium constants of reactions (1) and (2). It should be realised that the extent of proton and hydroxyl transfer is not a property of the oxide surface alone but reflects the *relative* affinities of the solvent and solid for H^+ and OH^-, so that $p\mathrm{H}^\circ$ depends on the nature of the liquid as well. In the present study only aqueous systems will be discussed.

Is it allowed to convert the σ_0 (pH)-curves into σ_0 (ψ_0)-curves, where ψ_0 is the surface potential, related to pH via Nernst' law

$$\psi_0 = \frac{RT}{F}\,(p\mathrm{H} - p\mathrm{H}^\circ) \qquad (4)$$

This is open to question. The reason can be traced by rederiving (4) for an oxidic surface. For the sake of argument, let H^+ be the potential-determining ion, then in equilibrium

$$\tilde{\mu}^{S}_{H^+} = \tilde{\mu}^{L}_{H^+} \qquad (5)$$

if $\tilde{\mu}$ stands for electrochemical potential. $\tilde{\mu}^{L}_{H^+}$ is readily written as

$$\tilde{\mu}^{L}_{H^+} = \mu^{0L}_{H^+} + RT \ln a_{H^+} + F\,\Phi^{L} \qquad (6)$$

where Φ^L is the Galvani potential inside the liquid phase. Eq. (4) with $\psi_0 = (\Phi^S - \Phi^L) - (\Phi^S - \Phi^L)_{p.z.c.}$ now follows from (5) and (6) if $\tilde{\mu}^{S}_{H^+}$ may be replaced by $(\mu^{0S}_{H^+} + F\,\Phi^S)$. This substitution is only valid if the chemical potential $\mu^{S}_{H^+}$ is independent of the activity of H^+ on the surface. This is unlikely, because H^+ is not a constituent of the solid and its adsorption will modify the composition of the surface layer. For this reason, we shall not convert the pH-axis into a potential axis. In order to do so an assumption must be made concerning the dependence of $\mu^{S}_{H^+}$ on Γ_{H^+}. For a substance like silver iodide, this difficulty does not occur, because the potential-determining ions (Ag^+ and I^-) are constituents of the solid and their adsorption does not lead to changes in composition. Hence in this case the pAg or pI axis can be replaced by a ψ_0 axis.

3. *Surface Charge Curves on Oxides Compared with those on Silver Iodide and Mercury*

In Fig. 1 the surface charge on some oxides is compared with those on mercury and silver iodide. In order to facilitate the comparison all curves are drawn with respect to their respective points of zero charge. $\Delta pH = pH - pH^{o}$. The indifferent electrolytes chosen show little or no specific adsorption. The salt concentration is chosen as 0.1 *M* so that the double layer is mainly non-diffuse, (any difference between different materials would show up most clearly in the non-diffuse part of the double layer).

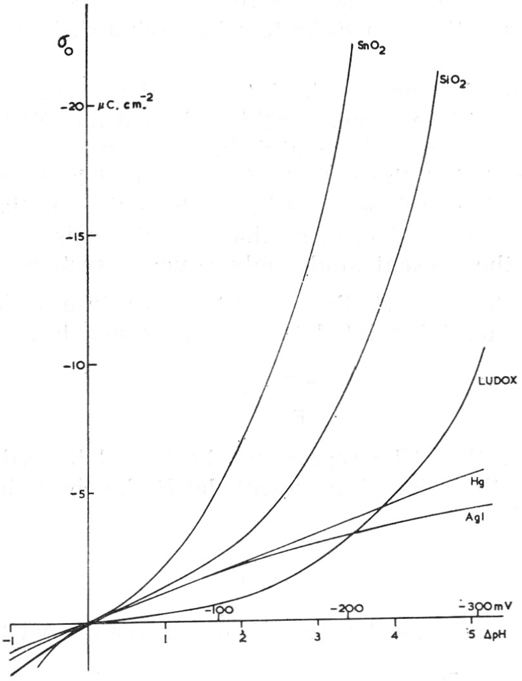

Fig. 1. Surface charge curves for oxides, compared with mercury and silver iodide. The sources are: SnO_2, natural cassiterite: Ahmed and Maksimov[3], 10^{-1} *M* KCl; SiO_2 precipitated silica: Tadros and Lyklema[4], 10^{-1} *M* KCl; Ludox, colloidal silica (could contain admixture of Al_2O_3): Bolt[34], 10^{-1} *M* NaCl, (calc. assuming $pH^{\circ} = 3.5$); Hg, Grahame[5], 10^{-1} *M* NaF (after integration of differential capacitance); AgI, Lyklema[6], 10^{-1} *M* KNO_3.

The figure shows that the shapes of the σ_0 (*p*H)-curves for the three oxidic materials chosen are quite different from those on mercury and silver iodide, whereas between the latter two only small differences are found. For Hg and AgI, the curves are slightly concave towards the potential axis, but for oxides the charge increases progressively with increasing *p*H. This applies not only to the three examples of Fig. 1 but is a general feature that all oxides have in common. Similar types of curves have also been found for Al_2O_3[7,8], Fe_2O_3 (hematite and goethite)[1,3,9,10], MnO_2[11], ZnO[12] and TiO_2 (rutile)[3,13].

The total amount of charge that can be accommodated on an oxide surface depends strongly on the nature of the surface. That the notion »nature of the surface« should be taken in the wider sense of the word, *i. e.* not restricted to chemical differences only is shown by Fig. 2 in which some σ_0 (*p*H) curves are drawn for some oxides all having a SiO_2-basis, but differing in other respects. It is important to consider the relative magnitudes of σ_0 in these systems in some more detail.

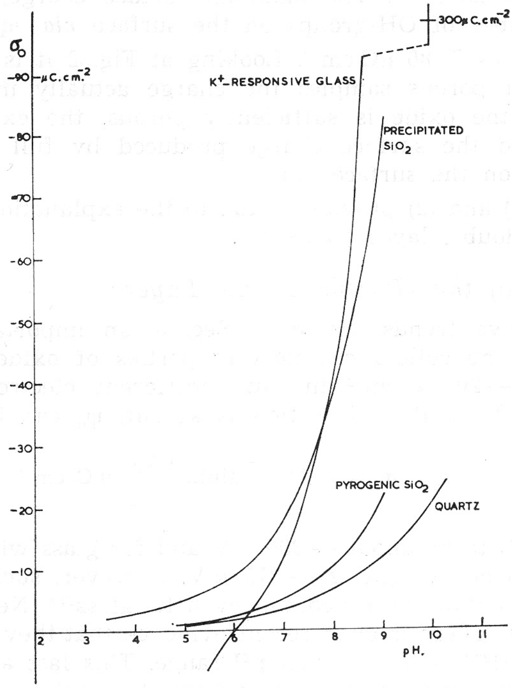

Fig. 2. Surface charge — *p*H curves for four silica-type oxides. The sources are: Glass, K^+ — responsive: Tadros and Lyklema[14], 10^{-1} *M* KCl; SiO_2, precipitated, Tadros and Lyklema[4], 10^{-1} *M* KCl; SiO_2, pyrogenic, Abendroth[15], 10^{-1} *M* KCl; Quartz (Brazilian), Li and De Bruyn[16], 10^{-1} *M* NaCl.

The pyrogenic SiO_2, used by Abendroth was, according to the author, a non-porous Cab-O-Sil. Quartz is also non-porous, although there may be small crevices on the surface due to the grinding. Using the *t*-plot technique the precipitated SiO_2, studied by Tadros and Lyklema[4], was shown to be porous. The glass was K^+-responsive, that is to say, if made into a glass-electrode it responds to K^+ over several decades of *p*H. Besides SiO_2, it contains as admixtures 12.4 mole % of B_2O_3, 12.0% of K_2O, 1.26% of GeO_2 and 1.30% of Al_2O_3 which tend to make it more basic as reflected in the relatively high p. z. c (pH^0 ~ 6.0). Before use, the crushed glass powder was soaked for a prolonged period, leading to a leaching of the superficial layers. As a result, the glass surface has a very open structure. In the field of glass-electrode electrochemistry this layer is usually referred to as »surface gel layer« or »swollen layer«. For our purpose it is important that the glass possesses a very porous surface layer. Comparing the four curves of Fig. 2, the following trend is manifest: the more porous the surface, the higher the surface charge at given Δ *p*H. (1).

Let us now look at the absolute magnitude of σ_0 in connection with the density of OH-groups on the surface. This number can be determined by independent techniques, *e. g.* from analysis of H_2O-adsorption isotherms, or from chemical reactions. It depends on the nature of the silicate surface how many of these groups are found but there are of the order of 5 OH per mμ^2, that is one OH per 20 Å^2 [17–19]. For hematite, Jurinak finds a very similar value, namely 22—23 Å^2 [20]. The maximal surface charge, being determined by the total number of OH-groups on the surface *via* equations (1) and (2) follows from this as $\lesssim$ 80 μC cm^{-2}. Looking at Fig. 2 it is clear that at least for the two most porous samples the charge actually measured is higher. We conclude: if the oxide is sufficiently porous, the experimental surface charge can exceed the surface charge produced by full dissociation of all hydroxyl groups on the surface. (2)

The trends (1) and (2) provide a clue to the explanation of the properties of the electrical double layer on oxides.

4. The Concept of the »Porous Double Layer«

Besides the two trends, found in Sec. 3, an important third fact can be derived from the colloid chemical properties of oxides. If at a surface charge of (say) — 20 μC cm^{-2} in low indifferent electrolyte concentration (say 10^{-3} *M* KNO_3) specific adsorption is absent, ψ_d can be calculated from

$$-\sigma_0 = \sigma_d = 11.72\,\sqrt{c}\,\sinh.\frac{e\,\psi_d}{2\,kT}\ \mu\,\mathrm{C\ cm^{-2}} \qquad (7)$$

(with c in Mol. l^{-1}) to be about — 300 mV and for glass with $\sigma_0 = 300$ μC cm^2 ψ_d would have to be as high as — 375 mV. However, such high values of ζ are never experimentally observed, not even for glass[21]*. Neither are SiO_2-sols particularly stable. There is even recent evidence that they become less stable with increasing *p*H[22,23] over a given *p*H-range. This last argument especially leads to the conclusion: *that the high surface charge does not show up in the colloid chemical properties.* (3)

These three considerations have led us to postulate the concept of the porous double layer[25], the quintessence of which is that the surface charge as well as part of the countercharge is not restricted to the surface proper, but can be accommodated *also behind this surface,* because the surface layer is »porous«, or permeable to these ions. The more readily the surface layer is accessible, the higher may the experimental charge per cm^2 be. Fig. 3 gives a schematic picture of this model.

The porous double layer picture accounts at least qualitatively for the three trends arrived at above because:

(1) the better the ions can penetrate the more charge can be accommodated per cm^2,

(2) sorption not being restricted to the surface proper, experimental charges exceeding those corresponding to the number of OH-groups on the surface are possible and

(3) because counterions penetrate the surface as well, charge and potential at the solution side remain low.

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* ζ — potentials *can* be lower than ψ_d because the slipping layer does not coincide with the O. H. P., due to an appreciable visco-electric effect[24].

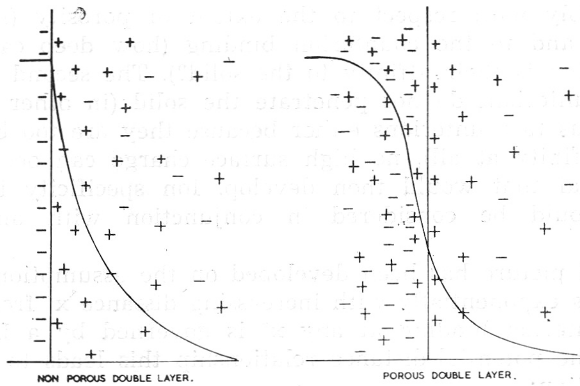

Fig. 3. Charge and potential in a porous and a non-porous double layer compared. The high surface excess of negative groups in a porous double layer does not lead to a high charge or high potential at the solution side of the double layer. In this simplified picture no Stern-layer is thought to be present. There tends to be a linear stretch in the potential-distance relationship inside the solid

Two remarks can be made at this point. In the first place, we have assessed the porosity of a surface form its ability to adsorb water and other vapours in its pores, whereas in the porous double layer model it is the porosity with respect to OH^- and (say) K^+-ions that counts. As a first approximation these two porosities may run more or less parallel (this follows also from Fig. 2) but there may exist surfaces that are impermeable to water vapour but still allow the uptake of OH^- and/or K^+, for example if a slow diffusion of these ions in conjunction with exchange with groups in the solid occurs.

The second remark is a direct consequence of this. The porous double layer model is not restricted to surfaces that are porous in the sense of gas adsorption but applies also to polyelectrolytes and latices. For example, the quantitative treatment (Sec. 5) is indeed reminiscent of that for polyelectrolytes, see *e. g.*[26–28].

An alternative idea to account for the very high surface charges has been forwarded by Bérubé and De Bruyn[29]. These authors seek an explanation in terms of the structure of the aqueous layer immediately adjacent to the oxide surface. The main postulate is that the hydroxyl ions are placed not on or in the surface, but remain in the solution, separated from the solid surface by at least one molecular layer of water. This model can not easily explain trends (1) and (3) mentioned above and a quantitative elaboration was not given. Some *ad hoc* explanations have been put forward with regard to the ion specificity, but it will be shown below that this feature also can be very well accounted for by the porous double layer model. We shall therefore pay no further attention to this alternative model although it is good to be aware of possible structural contributions.

5. *Porous Double Layers. Quantitative Aspects and Counterion Specificity*

In order to develop a quantitative theory for the charge and potential distribution in a porous double layer, some model assumptions have to be made first, notably with respect to the extent of porosity (how deep can ions penetrate?) and to the counterion binding (how deep can counterions penetrate and what is their affinity to the solid?). The second factor is very important: if counterions do not penetrate the solid (in other words, if the solid is not porous to counterions either because they are too big or because they have no affinity at all), no high surface charge can occur because of the high potential that would then develop. Ion specificity is therefore a feature that should be considered in conjunction with any theoretical interpretation.

A theoretical picture has been developed on the assumptions that (1) the porosity decreases exponentially with increassing distance x^s from the surface and (2) the counterion binding at any x^s is governed by a Langmuir-type equation[25]. For the potential-distance relationship this leads to the following differential equation:

$$\frac{d^2y}{du^2} = \frac{\alpha\, e^{-u}}{1 + Be^y} \tag{8}$$

in which y is the dimensionless potential $\frac{e\,\psi}{k\,T}$ in the solid, u is the dimensionless distance ax^s, where a is a quantity with the dimension $[\mathrm{cm}]^{-1}$, which is lower, the deeper is the penetration.

$$\alpha = \frac{4\,\pi\, e^2\, z n_-\,(o)}{\varepsilon\, kT\, a^2} \tag{9}$$

with z = valency of the counterion and n_- (o) is the number of negative groups per cm^2 on the surface ($x^s = o$). B reflects the affinity of the counterion to the solid

$$B = x_{salt}\, \exp.\, (\Phi/kT) \tag{10}$$

if x_{salt} is the mole fraction of the electrolyte in bulk and Φ is here the specific adsorption potential of the counterion under consideration. Eq. (8) is the Poisson-Langmuir equation. It replaces the Poisson-Boltzmann equation of the diffuse double layer theory to which it reduces in the limiting case of very low B. Computer solutions of (8) show y (o) to be exponential so long as y is low (as in the case of diffuse double layers) but y (u) becomes *linear for high potentials* (see Fig. 3), from which, using Poisson's law

$$\varrho = -\frac{\varepsilon}{4\,\pi}\,\frac{d}{dx^s}\left(\frac{d\psi}{dx^s}\right) \tag{11}$$

it may be deduced that, once the potentials are high, there is no more increase of ϱ. In other words, every adsorbing OH^--ion is then accompanied by a K^+-ion.

This feature follows also from another important equation of the quantitative theory, relating the penetrated countercharge σ_m to the surface charge, σ_o

$$\frac{\sigma_m}{\sigma_o} = B \int_o^{\infty} \frac{e^{y-u}}{1 + Be^y}\, du \tag{12}$$

Again, this integral defies analytical solution. However, it can be readily seen that if there is extensive counterion penetration (high B) $\sigma_m/\sigma_o \rightarrow 1$, implying that but little charge is left for the diffuse part of the double layer. Quantitative examples are given in ref. 25.

The conclusion that in sufficiently porous double layers σ_m/σ_0 approaches unity ties up very well with experimental experience. In 10^{-3} M solutions of (1—1) electrolytes, ζ-potentials tend to be not higher than about 125 mV, corresponding to an electrokinetic charge of only 2.2 μC cm^{-2}, at any rate far below σ_0 (Fig. 2). In the extreme case (glasses) σ_m/σ_0 can be as high as 0.99, a conclusion to which we shall revert in Sec. 6.

Let us now look at the counterion specificity. The theory predicts that at given pH σ_0 must be the higher, the more countercharge can be taken up by the surface, that is: the more porous for counterions is the surface. Thinking in terms of pure physical adsorption the expected lyotropic order for alkali-ions is

$$\sigma_0\,(\mathrm{Li}^+) < \sigma_0\,(\mathrm{Na}^+) < \sigma_0\,(\mathrm{K}^+) < \sigma_0\,(\mathrm{Rb}^+) < \sigma_0\,(\mathrm{Cs}^+) \tag{13}$$

because the hydrated radius decreases from left to right. This order has indeed been found for SiO_2[4]. However, not all oxides show the same order. Careful experiments by Breeuwsma[1,30] have shown that for hematite definitely

$$\sigma_0\,(\mathrm{Li}^+) \gg \sigma_0\,(\mathrm{K}^+) \sim \sigma_0\,(\mathrm{Cs}^+) \tag{14}$$

Hematite is less porous than the silica, used in ref. 4, so this trend shows up only if many experimental precautions are taken. Atkinson *et al.*[9] did not report this. Fig. 4 gives Breeuwsma's results in 10^{-1} M KCl, or LiCl. The uptake

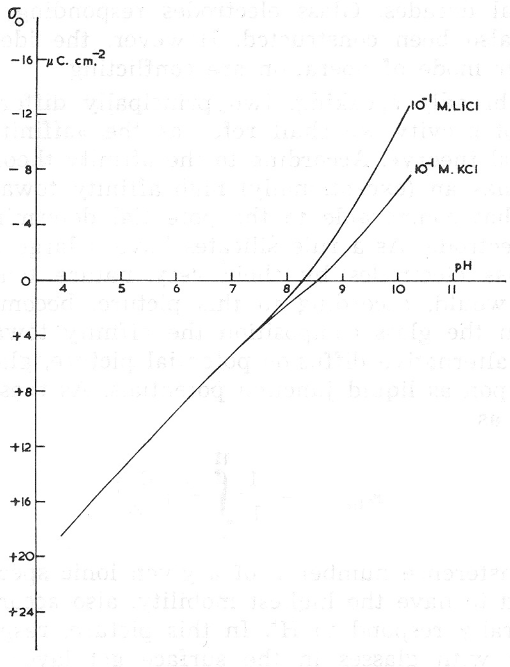

Fig. 4. The electrical double layer on hematite (α — Fe_2O_3). Influence of the nature of the counterion. Results by Breeuwsma.

of lithium is seen to be so strong as even to shift the p. z. c. The probable reason for preferential uptake of Li^+ over the other alkali-ions is that the crystal ionic radius of lithium (0.68 Å) happens to be almost identical to that of Fe^{3+} (0.64 Å). It is likely that Li^+ ions can occupy Fe^{3+}-sites. Here we have an example where the solid is porous towards a counterion but not to water. The other alkali ions are far too big to occupy one of the Fe^{3+}-sites, and any residual specificity must be ascribed to Stern-layer differences.

This picture is supported for hematite with earth alkali counterions. In this case σ_0 (Mg^{++}) is again definitely higher than σ_0 in the presence of all other ions ($r_{Mg^{++}}$ = 0.65 Å).

It must be expected that also for other oxides where the radius of the metal ion is around 0.65 Å, lithium is preferentially adsorbed. For TiO_2 (rutile), r_{Ti} = 0.68 Å, Bérubé and De Bruyn[29] report that in this case σ_0 (Li^+) is the highest in the alkali series, but they give no original data.

Thus it may be concluded that for porous double layers the lyotropic sequence in the surface charge may be either way, depending on the specific relationships existing between surface and counterion. High quality work in this field would be very welcome to check if the ideas ventilated above deserve wider attention, or should perhaps be replaced by a completely different picture.

6. *The Operative Mechanism of Glass Electrodes*

By way of application of the above a short discussion will now be given on the operative mechanism of glass electrodes.

That glass electrodes can behave as reversible H^+-electrodes has been known for several decades. Glass electrodes responding to Na^+ or K^+ and other ions have also been constructed. However, the ideas that have been developed on their mode of operation are conflicting.

There exist, broadly speaking, two principally different approaches, to which for sake of brevity we shall refer as the »affinity theory« and the »diffusion potential theory«. According to the affinity theory a glass responds to that ion that has an (exceptionally) high affinity towards the glass. This picture is somewhat comparable to the potential determining mechanism of a silver iodide electrode. As a rule silicates have a large affinity for H^+ and OH^-, so that glass electrodes by their very nature tend to be hydrogen electrodes. They would, according to this picture, become Na^+-electrodes if due to changes in the glass composition the affinity towards Na^+ would be enhanced. In the alternative diffusion potential picture, glass electrode potentials are looked upon as liquid junction potentials. As these potentials can be generally written as

$$E_{diff} = -\frac{1}{F}\int_{I}^{II} \sum_i t_i \frac{d\mu_i}{z_i} \tag{15}$$

it is now the transference number t_i of a given ionic species that counts. As protons are bound to have the highest mobility, also according to this theory glasses will generally respond to H^+. In this picture, response to Na^+ would be expected only with glasses in the surface gel layer of which Na^+-ions would be very mobile.

Hitherto it has not been possible to discriminate between these two proposed mechanisms, partly because it is extremely difficult to measure affinities and/or transference numbers in surface layers, partly because both theories give equally satisfactory equations for the electrode potential as a function of the concentrations of the ions to which it responds (*e. g.* H^+ and Na^+)[31].

It then occured to us, that at least one aspect could be verified on the basis of the ideas of the porous double layer, developed above. If the affinity picture applied, one would find a definite preference of the glass towards Na^+ over other alkali-ions at fixed *p*H under the conditions where the glass responds to Na^+. And as for glasses $\sigma_0 \sim \sigma_m$ (Sec. 5), this would lead to a higher surface charge in Na^+ — solutions compared with solutions of the other alkali metal salts. As σ_0 is a measurable quantity (after grinding of the glass) one thus has a means for discriminating between the two interpretations.

The surface charge determinations have been performed for a Na^+- and for a K^+-responsive glass[14]. Part of the σ_0 — *p*H curve in 10^{-1} *M* KCl is shown in Fig. 2. It appeared that there was no preference whatsoever for the ion to which the glass responds in the case of Na^+-responsive glass, whereas some specificity was found for K^+-responsive glass, however with σ_0 being *lowest* in KCl, as compared to other alkali chlorides. For example in 10^{-1} *M* LiCl at $pH = 8.5$ $\sigma_0 = 145$ $\mu C\ cm^{-2}$, almost twice as high as in KCl (Fig. 2). So generally response and affinity are not related at all.

If these two experiments are supported by other ones, it would lead automatically to the conclusion that glass electrode potentials are diffusion potentials and not potentials based on something like preferential affinity.

This conclusion, in turn is of great importance for the further technical development of glass electrodes. For example, although silicate groups have an appreciable affinity towards Ca^{2+} this does not lead to Ca^{2+}-response because the mobility of Ca^{2+}-ions in this type of structure is quite low[32,33]. On the other hand, membrane electrodes or »leaking« solid electrodes can be successfully applied because transference of Ca^{2+} is possible.

This application, as well as the possibility of applying the porous double layer model to latices and (bio) polyelectrolytes suggests that further studies in this field could lead to interesting discoveries.

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IZVOD

Električki dvosloj na oksidima

J. Lyklema

Svojstva električkog dvosloja na oksidima kritički su prikazana time što su uspoređeni podaci iz literature za dvosloj na živi, argentum-jodidu i na različitim oksidima. Postojanje visokog površinskog naboja na mnogim oksidima u kontaktu s elektrolitnom otopinom objašnjava se dvjema najvažnijim teorijama. Prva, po Bérubé i de Bruynu, postulira odstojanje ravnine najbližeg pristupa potencijalno determinantnih iona (OH^-) od same čvrste površine. Druga teorija, koju daje autor, zasniva se na ideji poroznog dvosloja. Taj model dozvoljava difuziju iona u samu površinu i nagomilavanje naboja ispod čvrste površine. Modelom poroznog dvosloja moguće je objasniti i obrat liotropnog niza koji je opažen na nekim oksidima (npr. hematitu), a isto tako i svojstva ionski-specifičnih staklenih elektroda.

LABORATORY FOR PHYSICAL AND COLLOID CHEMISTRY
AGRICULTURAL UNIVERSITY
WAGENINGEN, NETHERLANDS

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