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The ZnO/Aqueous Solution Interface

I. Capacity of the Double Layer¹

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At the ZnO/aqueous electrolyte solution interface, three processes occur on changing the pH of the medium: (a) adsorption of H^+ or OH^- ; (b) dissolution or precipitation of ZnO; (c) a slow process consuming H^+ or OH^- . A technique is described by which these processes can be separated. When due allowance is made for the slow process and when the influence of changes in solubility is eliminated, the capacity due to adsorption of H^+ or OH^- alone can be calculated: it is significantly smaller than that found by titration, and smaller than that of the diffuse double layer. The Stern capacity is comparable to that found at AgI/aqueous electrolyte solution interfaces near the pzc.

INTRODUCTION

Many model concepts in colloid chemistry have been developed at Hg/electrolyte solution interfaces or AgI/electrolyte solution interfaces. When applying these model concepts at oxide/electrolyte solution interfaces, frequently difficulties are encountered. Thus, Blok and de Bruyn (1-4) found by "titration" experiments, a capacity at the ZnO/aqueous solution interface surpassing the diffuse double layer capacity as calculated from the Gouy-Chapman theory (5). When applying the usual formula for evaluating the Stern capacity:

$$\frac{1}{C_{st}} = \frac{1}{C_{total}} - \frac{1}{C_{diff}} \quad [1]$$

(where C_{st} = the Stern capacity and C_{diff} = the diffuse layer capacity), the Stern capacity would become negative.

This phenomenon can be explained by assuming chemisorption or strong physical specific adsorption. In that case for a model where, in agreement with Stern's ideas, the

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inner and outer Helmholtz planes coincide,

$$\begin{aligned} \frac{1}{C_{total}} &= \frac{d\psi_0}{d\sigma_0} = \frac{d(\psi_0 - \psi_d)}{d\sigma_0} + \frac{d\psi_d}{d\sigma_0} \\ &= \frac{1}{C_{st}} + \frac{d\psi_d}{d\sigma_d} \times \frac{d\sigma_d}{d\sigma_0} \\ &= \frac{1}{C_{st}} - \frac{1}{C_{diff}} \times \frac{d(-\sigma_\beta - \sigma_0)}{d\sigma_0} \\ &= \frac{1}{C_{st}} + \frac{1}{C_{diff}} \times \left(1 + \frac{d\sigma_\beta}{d\sigma_0}\right) \quad [2] \end{aligned}$$

where

σ_β = the charge per unit surface area in the Stern layer,

ψ_d = the potential in the Stern layer,

σ_0 = the charge per unit surface area on the solid,

σ_d = the charge per unit surface area in the diffuse double layer, $\sigma_0 + \sigma_\beta + \sigma_d = 0$,

$C_{diff} = -d\sigma_d/d\psi_d$.

In expression [2], $d\sigma_\beta/d\sigma_0$ will be <0 , and if its absolute value is large enough, C_{st} may be >0 , even if $C_{total} > C_{diff}$. The quantity $d\sigma_\beta/d\sigma_0$ would be a very interesting param-

eter, even if only a limiting value (necessary for making $C_{st} > 0$) could be determined.

In addition the "titration" capacity of the ZnO/aqueous solution interface differs considerably from the capacity as measured in an ac bridge (1), in contrast with results obtained for Hg/aqueous solution interfaces (6) and AgI/electrolyte solution interfaces (7).

Such problematic capacities are by no means restricted to ZnO as solid phase: similar data have been reported for TiO₂ (8) and Fe₂O₃ (9, 10). In view of the importance of oxides in many technological problems, it was thought worthwhile to elucidate the reasons for the discrepancies mentioned.

On changing the pH of an aqueous ZnO suspension, as during an experiment for measuring the capacity by titration, three processes should be taken into account: in addition to adsorption of H⁺ and OH⁻ ions at the interface, dissolution or precipitation of ZnO consumes H⁺ or OH⁻ ions; in addition a slow process has been reported (1, 3) which also consumes H⁺ or OH⁻ ions. Similar slow processes have been reported for TiO₂ (8), Fe₂O₃ (10), and MnO₂ (11) as solid phases. Blok tried to eliminate these processes by correcting for the amount of ZnO dissolved (1, 2) and by carrying out the titration experiments rapidly.

Our first aim was to differentiate as carefully as possible between these processes. The results of the ensuing capacity measurements are described in the present paper; in a second paper, a mechanism will be presented for the slow H⁺ or OH⁻ consuming process.

EXPERIMENTAL

Materials

(1) ZnO: three samples were used: (a) pro analysi, ex Merck: employed as received. The surface area as measured by a Ströhlein areameter (which is based on N₂ adsorption) (12) was 2.21 m² g⁻¹. The metal impurities (Pb, Cu, Fe, Mn, Cd, As, Ca) were (according to specification) 0.001% at most, among the foreign anions SO₄²⁻ was ≤0.005%,

Cl⁻ ≤ 0.001%, PO₄³⁻ ≤ 0.0005%, total N ≤ 0.001%. (b) ex Highways, as received. The surface area was 3.85 m² g⁻¹. The metal content was lower than that of sample a. (Fe, 3 ppm; Pb, 1 ppm; Si, 1 ppm; Cd, Ca, Cu, Mg < 1 ppm), but foreign anions were not detected. (c) sample b: after heating in air at 650°C and cooling *in vacuo*. The surface area was 2.07 m² g⁻¹. The sample was kept in a desiccator until shortly prior to use.

(2) Water: doubly distilled. Specific conductivity ~10⁻⁶ Ω⁻¹ cm⁻¹.

At the start of an experiment, dissolved CO₂ was removed by passing purified N₂ over the solution until the pH became constant (see later).

(3) Nitrogen: commercial N₂ was led successively through a Carbosorb bed, a washing bottle containing 1 M NaOH solution, and through two washing bottles containing water.

(4) NaCl: pro analysi ex Merck, dried at about 140°C.

(5) NaOH and HCl for titration experiments and for keeping the pH constant: pro analysi ex Merck (titrisol 9959 and 9973, respectively).

Apparatus

(1) Titration experiments: Corning nr. 113 pH meter, using an Orion 91-01-00 glass electrode and a 90-01 single junction reference Ag/AgCl electrode.

(2) Experiments at constant pH: Radiometer pH stat composed of a TTT 2 titrator extended by a two-way pH stat module, two SBR 2c recorders, and two ABU 1B autoburettes (one filled with 0.01 M HCl, the other with 0.01 M NaOH). The pH was registered independently of the pH stat by means of a Corning nr. 113 pH meter.

Procedure

(1) Continuous titration experiments: quantities of ZnO (sample b) ranging from 2 to 6 g were added to 100 ml NaCl solution (10⁻³, 10⁻², or 10⁻¹ M). Stirring was effected such as to keep all ZnO suspended; then the

pH was brought to 8.5. After waiting for 10 min, the pH was changed by 0.25 pH unit; it was kept constant for 3 min by NaOH or HCl addition. The time period of 3 min was chosen in agreement with Blok and de Bruyn (1, 2). Then the pH was changed by 0.25 unit again, etc. At any pH value, the total amount of NaOH or HCl added after 3 min waiting was registered. The titrations were carried out at 20°C in an atmosphere of purified nitrogen. At any pH, the total amount of HCl or NaOH required for one pH step of the titration was linearly extrapolated to zero amount of ZnO; the slope of the line was taken to be the amount of acid or alkali adsorbed per gram of ZnO. From the intercept of this line with the vertical axis, the "solubility" of ZnO at this particular pH can be calculated (see Ref. (2)).

(2) Experiments at constant pH: 300 ml NaCl solution (10^{-3} , 10^{-2} , or 10^{-1} M) in water was kept in a thermostatted beaker, which was colored black in order to eliminate any influence of light on the measurements. The solution was intensively stirred by a magnetic stirrer during the whole experiment. After adjusting the pH to the value required, purified nitrogen was passed over the solution, while the pH was kept constant by the pH stat. When no more acid or alkali was called for, 10–20 mg of ZnO was added in order to obtain a saturated solution. The attainment of solubility equilibrium as indicated by acid or alkali requirements took 1–14 hr, depending on the pH. Then 15 g ZnO was added, and the amounts of NaOH or HCl required for keeping the pH constant were registered continuously.

(3) The liquid phase in the experiments at constant pH was analyzed at predetermined times, after centrifugation, for Zn by a spectrophotometric method (13).

RESULTS

1. Titration Experiments

The adsorbed amounts of HCl or NaOH determined as described in the experimental

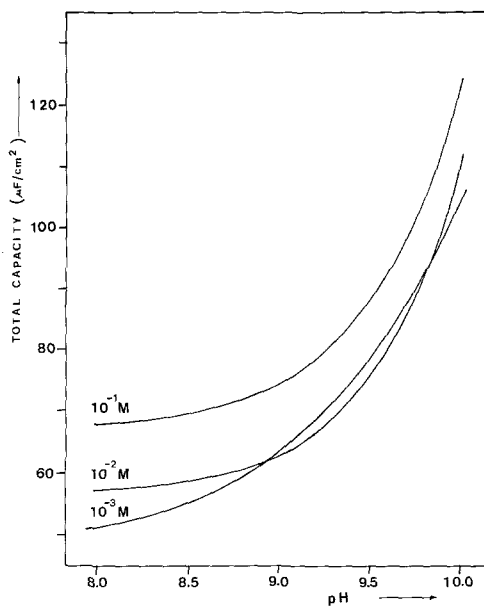


FIG. 1. Capacity of the double layer on ZnO, as determined by titration in NaCl solutions.

part were expressed as surface charges ($\mu\text{C cm}^{-2}$) and differentiated with respect to pH in order to obtain the capacities. Figure 1 shows the result. The capacities are seen to be of the same order of magnitude as those determined by Blok and de Bruyn (1–4). However, there are some differences: the titration curves did not, in our experiments, intersect each other at one pH, so that a determination of the pzc by the usual method (14) was impractical. Furthermore, it was found that the result is influenced strongly by the details of the experimental procedure employed during the titrations, in particular by the time of waiting before a new change in pH is effectuated and by the magnitude of the pH step between successive measurements. It appears to be necessary to follow the amount of acid or alkali required for keeping the pH constant more carefully.

2. Experiments at Constant pH

Figure 2 shows some typical results, obtained with ZnO sample b in 0.1 M NaCl

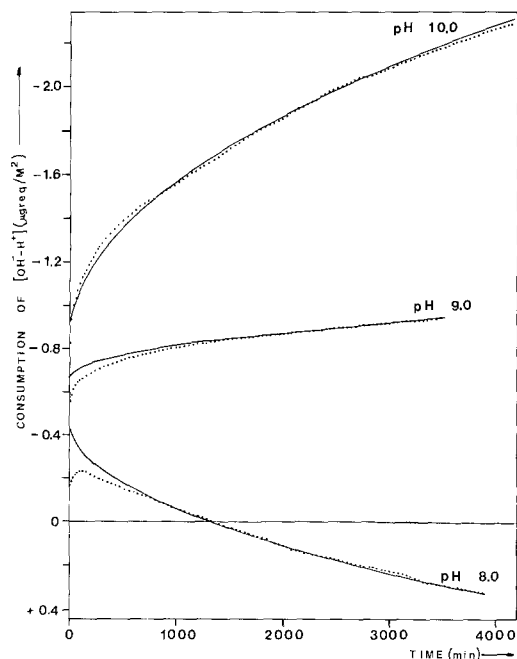


FIG. 2. Total amount of $[\text{OH}^- - \text{H}^+]$ consumed by ZnO since the first contact with 0.1 M NaCl solution at different pHs as a function of time. The full lines indicate the $t^{1/2}$ extrapolation to $t = 0$.

solution. The curves are rather complex, but if it is assumed that they consist of an initial and a "long run" reaction of which the former comes to a standstill after some time, the kinetics of the "long run" reaction can be obtained by analyzing the later parts of the curves. This long run reaction was found to consume H^+ ions at low pH, OH^- ions at high pH, the transition being situated at a $\text{pH} \approx 8.9$.

In all cases, the amount of H^+ or OH^- consumed by the slow reaction was proportional to the square root of the time and the onset of a $t^{1/2}$ dependence occurred after about 800–1000 min.

From these curves, the quantities of OH^- consumed by processes other than the slow reaction can be obtained by extrapolating the adsorbed amount $t^{1/2}$ relation to $t = 0$. A theoretical justification for this procedure, based on a mechanism for the slow reaction which accounts for all data available at present, is given in another paper

(15). The quantities obtained in this way are shown in Table I. They do not include any amounts of OH^- or H^+ consumed by changes in solubility of the ZnO, since the solutions were saturated toward ZnO by addition of a small amount of ZnO before introduction of a large amount necessary for adsorption measurements; moreover, the total quantity of Zn in solution remained constant during an experiment. The quantities of Zn in solution found by this method agree well with those calculated from thermodynamic data (2). On the other hand, the solubilities of ZnO, as determined during titration experiments, differ considerably from the calculated values, as had been found by Blok and de Bruyn.

Figure 3 shows the quantities of $[\text{OH}^- - \text{H}^+]$ consumed by the processes taking place on the first contact of ZnO with aqueous solution. At all pH values and all NaCl concentrations investigated, this "fast" process consumes a net amount of OH^- . The curves do not in the pH range investigated

TABLE I

Surface Charges σ_0 (C m^{-2}) on ZnO (Sample b) as Found by Extrapolation to $t = 0$, and Diffuse Layer Charges σ_{diff} (C m^{-2}) as Calculated from the ζ -Potential after 500 min Contact Time between ZnO and Aqueous Solution^{a,b}

pH	[NaCl] = 0.1 M ($\times 10^{-2}$)	[NaCl] = 0.01 M ($\times 10^{-2}$)		[NaCl] = 0.001 M ($\times 10^{-2}$)	
	σ_0	σ_0	σ_{diff}	σ_0	σ_{diff}
8	1.88	0.91	0.44		
8.3				0.18	0.33
8.5	0.04	0.14	0.28		
8.8				-0.04	0.20
9.0	-0.07	-0.22	0.13		
9.3				-0.25	0.08
9.5	-0.36	-0.65	0.17		
9.8				-0.57	0.13
10.0	-1.84	-1.30	0.23		
10.3				-1.01	0.17

^a Ref. (15).

^b For σ_0 , the surface charge at the pzc (pH 8.7) is taken as reference.

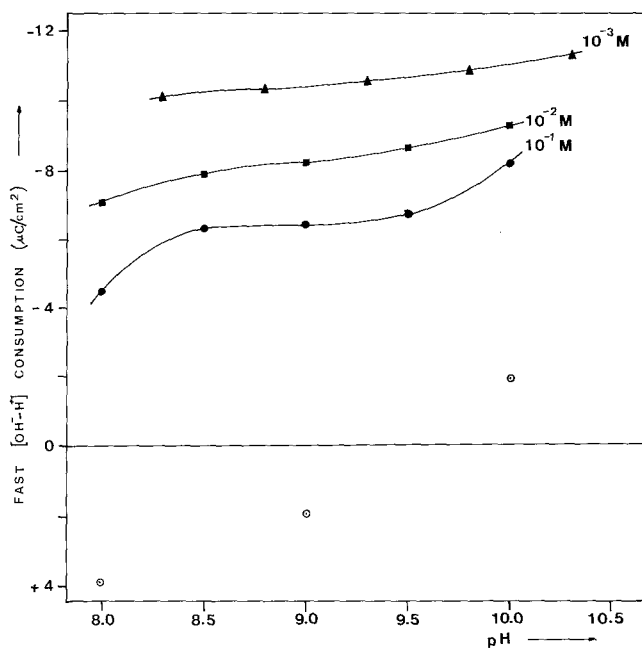


FIG. 3. Quantities of $[\text{OH}^- - \text{H}^+]$ consumed by ZnO in NaCl solutions during the "fast" process. ●, ■, ▲, sample b; ○, sample c in $10^{-1} M$ NaCl.

intersect at any particular pH value, which indicates strong chemisorption. In the present case, predominant chemisorption of anions (Cl^-) is evidenced by the ζ -potential (15), which is negative at all pH values and at all reaction times, even if the ZnO at pH = 8 finally has consumed more H^+ than it had first consumed OH^- (Fig. 2).

Pretreatment of ZnO by heating in air causes a general shift toward lower OH^- consumption, even toward H^+ consumption (Fig. 3). This difference is ascribed to carbonate ions on the surface of the ZnO as received, which are expelled upon heating (the slow reaction is not noticeably different for samples b and c). The data are too scanty for a reliable differentiation, although they indicate that heating effects only a downward shift of the σ_0/pH curve in Fig. 3 without influence on the capacity.

DISCUSSION

For oxides, H^+ and OH^- are generally considered to be potential determining ions

(16). However, it should be realized that this is true for ZnO in another sense than for, e.g., AgI: ZnO is an electronic conductor (17), and diffusion of the ions in the solid at room temperature is negligible.

The electrochemical potential of a lattice ion in the bulk solid therefore is not necessarily equal to the electrochemical potential of a lattice ion near the surface. It has been pointed out by Blok (1) that this implies that the potential difference between the bulk solid and its surface is not defined by the electrochemical potential of the lattice ions; it is determined by a space charge in the solid. However, for calculating double layer capacities from the adsorption of potential determining ions it is only important to know the relation between the surface potential ψ_s (i.e., the potential difference between the surface and the bulk solution) and a_{H^+} , the activity of the protons in the solution.

Usually, a Nernst relation

$$d\psi_s = RT/F \times d \ln a_{\text{H}^+} \quad [3]$$

is assumed. This follows, to be sure, from the equality of electrochemical potential of protons in solution, and at the surface:

$$\mu_{\text{H}^+}(\text{ads.}) = \mu_{\text{H}^+}^*(\text{ads.}) + f(\theta) + F\psi_s \quad [4]$$

where θ = the degree of occupation of the surface sites, if $f(\theta)$ is constant, i.e., if the chemical part of the electrochemical potential of adsorbed protons does not depend on θ . We investigated a possible influence of changes in θ on the validity of the Nernst equation as follows:

(1) A simple Langmuir-type dependency of $\mu_{\text{H}^+}(\text{ads.})$ on θ was introduced:

$$\mu_{\text{H}^+}(\text{ads.}) = \mu_{\text{H}^+}^*(\text{ads.}) + RT \ln (\theta/(1 - \theta)) + F\psi_s \quad [5]$$

with

$\theta = 0$ corresponding to complete dissociation of surface $\equiv\text{ZnOH}$ groups to $\equiv\text{Zn}-\text{O}^{(-)}$;

$\theta = 1$ corresponding to complete association of surface $\equiv\text{ZnOH}$ groups with H^+ to $\equiv\text{Zn}-\text{OH}_2^{(+)}$.

If all oxygen ions at the ZnO surface are converted into hydroxyl groups, a density of one $\equiv\text{ZnOH}$ per $8.5 \times 10^{-2} \text{ nm}^2$ is obtained; (density at the (0001) face: one per $9 \times 10^{-2} \text{ nm}^2$; at the (1000) face: one per $8.4 \times 10^{-2} \text{ nm}^2$). θ then ranges in our experiments between 0.495 (at pH 10, $[\text{NaCl}] = 0.1 \text{ M}$) and 0.505 (at pH 8, $[\text{NaCl}] = 0.1 \text{ M}$). Differences in $RT \ln (\theta/(1 - \theta))$ then are negligible compared with differences in $2.303 \times RT/F \times \text{pH}$.

(2) However, the Langmuir-type of dependency is applicable only if all sites are equal, and if interaction between protons adsorbed on neighbor sites is neglected. Taking into account that this interaction excludes all considerations assuming a random distribution of charged sites (18) or describing the adsorption of ions by one "surface potential," and postulating that all local deviations from this macropotential are either small or insensitive to changes

in the surroundings (18, 19). Both approximations have been shown to be unrealistic, at least for $\text{CaSiO}_3/\text{aqueous solution interfaces}$ (20). Neither can Levine and Smith's theory (21) be relied upon, since deviations from a random distribution are taken into account here either by a Flory-Huggins type of treatment (derived for the case where these deviations are due only to differences in size between different adsorbed species) or by the "discreteness of charge" effect (derived for the case that all places near the surface are equally accessible to all ions) (22). The latter assumption may be appropriate for the Hg/aqueous solution interface, but is much less so for oxide/aqueous solution interfaces, where the local potential is expected to vary considerably along the interface.

The effects causing deviation from the Langmuir dependency (relation 5) can be taken into account, however, by recognizing different types i of surface sites (20). To the chemical potential of a proton adsorbed on a site of type i , a value

$$\mu_{\text{H}^+i}(\text{ads.}) = \mu_{\text{H}^+i}^*(\text{ads.}) + RT \ln (\theta_i/(1 - \theta_i)) + F\psi_i \quad [6]$$

is awarded, where ψ_i = the local potential including interaction with other adsorbed ions; $\mu_{\text{H}^+i}^*(\text{ads.})$ is a function of temperature and pressure only.

The local potential must be taken such as to make $e_0\psi_i$ the electrostatic work necessary for bringing a H^+ ion to the site; i.e., it is the potential at the site exclusive of the potential due to an adsorbed H^+ ion.

Of course, use of this formula implies a random distribution of vacant and occupied sites of type i ; this is justified since the sites of this type are not in general situated close together but are spread all over the surface. Thus, the situation at one particular site of type i is not noticeably influenced by the degree of occupancy of the other sites of the same type.

In the case of ZnO, a vacant site is considered to be a $\equiv\text{Zn}-\text{O}^{(-)}$ group. Accord-

ing to [6]

$$\theta_{iH} = \frac{a_H \exp(u_i)}{1 + a_H \exp(u_i)} \quad [7]$$

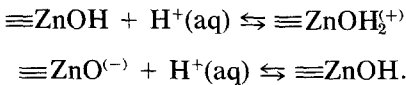
with u_i = the (dimensionless) total adsorption energy = $(\mu_{iH}^*(sol) - \mu_{iH}^*(ads) - F\psi_i)/RT$. This gives the degree of occupancy of a site, if only one H^+ ion could become adsorbed. However, in the case of ZnO, two H^+ ions can be accommodated on one site, with the second, however, much more difficult to become adsorbed than the first one. The total amount of H^+ ions on sites of type i is then determined by

$$\beta_{iH} = \frac{1}{2} \left[\frac{a_H \exp(u_i)}{1 + a_H \exp(u_i)} + \frac{a_H \exp(u_i + \Delta u_i)}{1 + a_H \exp(u_i + \Delta u_i)} \right] \quad [8]$$

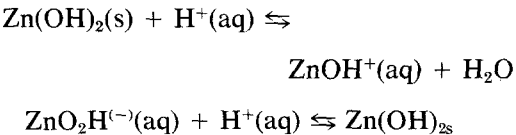
where

$\beta_{iH} = 0$ if all $\equiv ZnOH$ groups of type i are converted into $\equiv ZnO^{(-)}$ groups;
 $\beta_{iH} = 1$ if all $\equiv ZnOH$ groups of type i are converted into $\equiv ZnOH_2^{(+)}$ groups
 $\Delta u_i = \ln(K_2/K_1)$.

K_1 and K_2 are the association constants for the reactions:



In the present work, K_2/K_1 is estimated from known thermodynamic data (23) for the equilibria



which gives $\Delta u_i = -35.4$. The total amount of H^+ adsorbed is then given by

$$\Gamma_H = \sum_i \beta_{iH} N_{iH} = \int_{-\infty}^{\infty} \beta_{iH} N_{iH} du_i \quad [9]$$

if N_{iH} , the number of adsorption sites for H^+ of given total adsorption energy u_i , is

given as a function of u_i by a normalized distribution, e.g., a Gauss one:

$$N_{iH} = \frac{N_s}{w(2\pi)^{1/2}} \exp\left(-\left(\frac{u_i - f}{w2^{1/2}}\right)^2\right) \quad [10]$$

where f is the number average value of u_i ($=\mu_{iH}^*(sol) - \bar{\mu}_{iH}^*(ads) - F\bar{\psi}_i)/RT$), and w the standard deviation of the distribution. N_s is the total number of sites for H^+ ions, both occupied and vacant, per unit surface area; thus:

$$N_s = \equiv ZnOH + \equiv ZnO^{(-)} + \equiv ZnOH_2^{(+)}$$

It can be derived then (see Appendix) that an average value for $d\psi/dpH$ at the adsorption sites for H^+ ions can be calculated from:

$$\begin{aligned} \frac{F}{RT} \frac{d\bar{\psi}}{dpH} &= -2.303 - \frac{\frac{d\Gamma_H}{dpH}}{\int_{-\infty}^{\infty} N_i \left(\frac{\partial \beta_{iH}}{\partial u_i}\right)_{pH} du_i} \quad [11] \end{aligned}$$

The integral in [11] can be calculated at the pzc ($pH = 8.7$, see later) for any given value of w as follows: f in [10] is adjusted such as to make

$$\frac{1}{N_s} \int_{-\infty}^{\infty} \beta_{iH} N_{iH} du_i = \frac{1}{2}$$

at

$$a_H = 10^{-8.7} \quad (\beta_{iH} \text{ according to [8]}).$$

With the then known combination of w and f values, $1/N_s \int_{-\infty}^{\infty} N_i (\partial \beta_{iH} / \partial u_i)_{pH} du_i$ can be evaluated numerically. For the Δu_i value accepted, the integral is found to be = 0.01–0.013, at least for $11 < w < 30$ (this result is not strongly dependent on Δu_i). Since this is the standard deviation range expected (if all $\mu_{iH}^*(ads)$ would be equal, it would correspond to a standard deviation in the local potential between 2.5 and .75 V), the integral in [11] is taken to be about 0.012 here.

With the values for $d\Gamma_H/dpH$ calculated from Table I, the correction to the Nernst equation becomes about 10% at the pzc.

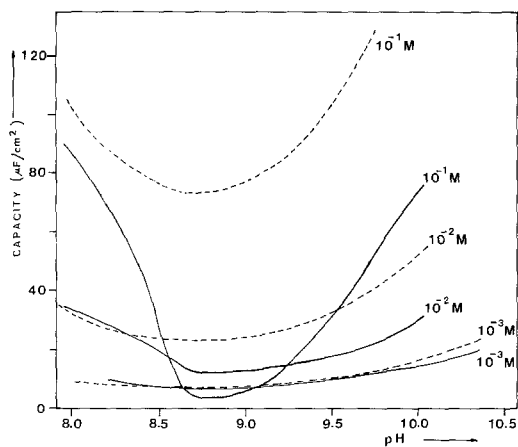


FIG. 4. Capacities of the double layer at the ZnO/aqueous NaCl solution interface from the data of Fig. 3 (—) and calculated from the Gouy-Chapman theory (----).

Since the experimental uncertainty of the capacity is rather large, we will neglect this correction near the pzc.

However, near the ends of the pH range covered by our experiments (pH 8 or 10) the Nernst relation cannot be relied upon. In particular, the capacity

$$\frac{d\sigma}{d\psi} = \frac{d\sigma}{dpH} \times \frac{dpH}{d\psi} \quad [12]$$

as calculated from the Nernst equation is smaller than the real capacity ($d\sigma/dpH$ is experimentally determined, the absolute value of $dpH/d\psi$ is larger than corresponds with the Nernst equation). Thus, deviation from the Nernst equation cannot be invoked to explain the large capacities found by titration experiments (Fig. 1).

The capacities found after extrapolating the $\sigma(t)$ curves (Fig. 2) to $t = 0$ by $\sigma = At^{1/2}$ are shown in Fig. 4, together with the capacities calculated from the Gouy-Chapman theory. Since the adsorption isotherms do not intersect at the pzc (Fig. 3), we had to choose a pzc by another criterion. As such, the pH of minimum capacity was chosen; this was found at all NaCl concentrations investigated, at pH 8.7. For the correct-

ness of this criterion, see Breeuwsma and Lyklema (24) (for Fe_2O_3 as solid).

It will be remembered that in the same region (at pH 8.9) the transition occurs from a H^+ consuming slow reaction to an OH^- consuming one. The difference between both pH values is probably not significant in view of the uncertainty in the pzc.

Measurements at lower NaCl concentrations, where the adsorption isotherms should intersect, are prohibited in our case by the increasing difficulty of keeping the pH constant without a buffer, at lower NaCl concentrations.

It is seen, that at $[NaCl] = 10^{-1}$ and $10^{-2} M$, the capacities as calculated by the present method are smaller than the diffuse double layer capacities; at $[NaCl] = 10^{-3} M$, both capacities are about equal, but there the experimental data are rather uncertain because of the difficulty of keeping the pH constant. In fact, the capacities in Fig. 4 are comparable to those measured by Blok (1) in an ac bridge; this resolves one of the problems raised by Blok's work. Our titration capacities, on the other hand, are comparable to those reported by Blok (1, 2), but these may be in error because of the changing solubility of ZnO with pH changes (establishment of a saturated solution takes a couple of hours and may be assumed not to be realized during a titration), and because of the lack of correction for the slow process.

In order to calculate Stern capacities, $d\sigma_\beta/d\sigma_0$ must be known at $t = 0$. On the basis of the data available at present, this can be done only approximately: First we have to assume that ψ_β , the average potential in the chemisorption plane, be equal to the ζ -potential. σ_β can then, in principle, be calculated as $\sigma_0 - \sigma_{diff}$ (σ_{diff} can be calculated from an average potential in the chemisorption plane, since both anions and cations contribute to it; whereas it would be unjustified to assume that the adsorption of any particular ionic species be described by that average potential).

ζ -potentials of ZnO have been determined during the slow reaction in 0.01 and 0.001 M solutions (15), but only after 500 and 3800 min contact. In all cases investigated the ζ -potential does not change any more after 500 min contact. Our second assumption then is that this constancy of the ζ -potential extends throughout the period of the slow reaction, from $t = 0$ onward. The results are shown in Fig. 5. A change in $d\sigma_\beta/d\sigma_0$ is found near the pzc from values near -1 at $\text{pH} > \text{pH}_{\text{pzc}}$, to values of -1.26 and -1.56 at $\text{pH} < \text{pH}_{\text{pzc}}$, for 0.01 and 0.001 M NaCl solutions respectively.

The latter values of $d\sigma_\beta/d\sigma_0$ are surprisingly strongly negative, but this is caused by the fact that in the pH region concerned the ζ -potential *decreases* (becomes more negative) with decreasing pH. This fact can be understood as follows:

As soon as a decrease in pH is accompanied by a considerable increase in surface $\equiv\text{Zn}-\text{OH}_2^{(+)}$ groups, chemisorption of Cl^- ions is assisted by electrostatic attraction. The combined action of van der Waals' and electrostatic attraction results in super-equivalent adsorption of Cl^- ions.

The Stern capacities can now be calculated from relation [2]. The results are shown

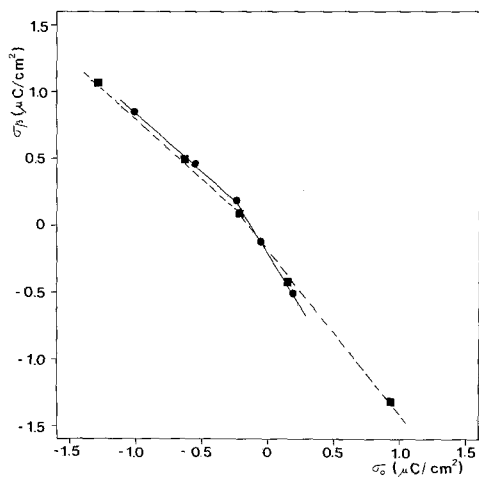


FIG. 5. σ_β ($= -\sigma_0 - \sigma_{\text{diff}}$) vs σ_0 for ZnO. σ_{diff} calculated on the basis of ζ -potentials (15). ■, 0.01 M NaCl; ●, 0.001 M NaCl.

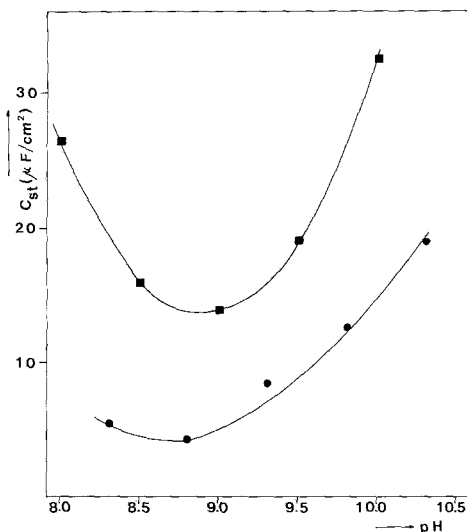


FIG. 6. Stern capacities for ZnO: ■, 0.01 M NaCl; ●, 0.001 M NaCl.

in Fig. 6. These Stern capacities are strikingly small in view of the pronounced chemisorption. It should be realized, however, that the assumptions introduced for their calculation introduce an element of uncertainty, although their trend (both as a function of pH, and as a function of electrolyte concentration) is in the expected direction.

CONCLUSION

Contradictions between the capacities at ZnO/aqueous NaCl solution interfaces determined by different methods can be resolved by correcting for a slow process consuming H^+ and OH^- ions.

APPENDIX

Deviation of a Relation between $d\bar{\psi}/dpH$ and $d\Gamma_H/dpH$

We describe adsorption of H^+ on ZnO as taking place on sites. A vacant site is taken to be a $\equiv\text{Zn}-\text{O}^{(-)}$ group at the surface; it can accommodate one or two H^+ ions. The total occupancy of the sites of type i (characterized by the total adsorption energy u_i) is given by relation [8].

The total amount of H^+ ions adsorbed is given by:

$$\Gamma_H = \sum_i \beta_i N_i = \int_{-\infty}^{+\infty} \beta_i N_i du_i \quad [13]$$

where $N_i(u_i)$ is given as a normalized distribution such as [10]. The change of Γ_H with $\gamma_H m_H$, the H^+ activity in the solution, is then given by:

$$\frac{d\Gamma_H}{d \ln \gamma_H m_H} = \int_{-\infty}^{+\infty} N_i \left(\frac{\partial \beta_i}{\partial \ln \gamma_H m_H} \right)_{u_i} du_i + \int_{-\infty}^{+\infty} \beta_i \left(\frac{\partial N_i}{\partial \ln \gamma_H m_H} \right)_{u_i} du_i. \quad [14]$$

We write:

$$\left(\frac{\partial N_i}{\partial \ln \gamma_H m_H} \right)_{u_i} = - \left(\frac{\partial N_i}{\partial u_i} \right)_{\ln \gamma_H m_H} \times \left(\frac{\partial u_i}{\partial \ln \gamma_H m_H} \right)_{N_i}. \quad [15]$$

The first factor at the right side can be calculated from [10], the second one can be evaluated, if w is constant. Then, N_i constant means $u_i - f$ constant, therefore:

$$\left(\frac{\partial u_i}{\partial \ln \gamma_H m_H} \right)_{N_i} = \frac{df}{d \ln \gamma_H m_H} \quad [16]$$

and with $f = (\mu_{H^+}^*(sol) - \mu_{H^+}^*(ads) - F\bar{\psi}_i)/RT$ we obtain:

$$\frac{df}{d \ln \gamma_H m_H} = - \frac{F}{RT} \frac{d\bar{\psi}_i}{d \ln \gamma_H m_H} \quad [17]$$

(the $\mu_{H^+}^*(ads)$ values are considered to be independent of the pH, since the most pronounced influence of the surface charge on $\mu_{H^+}(ads)$ has been taken into account by the local potential ψ_i). $\bar{\psi}_i$ is the number average of the potential at the H^+ adsorption sites, as follows from the definition of f .

In analogy with [15] we write:

$$\left(\frac{\partial \beta_i}{\partial \ln \gamma_H m_H} \right)_{u_i} = - \left(\frac{\partial \beta_i}{\partial u_i} \right)_{\ln \gamma_H m_H} \times \left(\frac{\partial u_i}{\partial \ln \gamma_H m_H} \right)_{\beta_i}. \quad [18]$$

Here, $(\partial u_i / \partial \ln \gamma_H m_H)_{\beta_i} = -1$. Then, [14] becomes:

$$\frac{d\Gamma_H}{d \ln \gamma_H m_H} = \int_{-\infty}^{+\infty} N_i \left(\frac{\partial \beta_i}{\partial u_i} \right)_{\ln \gamma_H m_H} du_i + \frac{F}{RT} \times \frac{d\bar{\psi}_i}{d \ln \gamma_H m_H} \int_{-\infty}^{+\infty} \beta_i \left(\frac{\partial N_i}{\partial u_i} \right)_{\ln \gamma_H m_H} du_i. \quad [19]$$

The absolute magnitudes of the two integrals at the right side are equal, because

$$\int_{-\infty}^{+\infty} \beta_i \left(\frac{\partial N_i}{\partial u_i} \right)_{\ln \gamma_H m_H} du_i = \int_{u_i=-\infty}^{+\infty} \beta_i dN_i = (\beta_i N_i)_{u_i=-\infty}^{+\infty} - \int_{u_i=-\infty}^{+\infty} N_i \left(\frac{\partial \beta_i}{\partial u_i} \right)_{\ln \gamma_H m_H} du_i \quad [20]$$

with $N_i = 0$, $\beta_i = 0$ for $u_i = -\infty$; $N_i = 0$, $\beta_i = 1$ for $u_i = +\infty$. Therefore, we write [19] as follows:

$$\frac{F}{RT} \frac{d\bar{\psi}_i}{d \ln \gamma_H m_H} = 1 - \frac{d\Gamma_H}{d \ln \gamma_H m_H} \int_{-\infty}^{+\infty} N_i \left(\frac{\partial \beta_i}{\partial u_i} \right)_{\ln \gamma_H m_H} du_i. \quad [21]$$

The condition $W = \text{constant}$, which has been applied in the foregoing, can be argued as follows: if the surface is covered either by $\equiv Zn-OH_2^{(-)}$ or by $\equiv ZnOH^{(+)}$ groups only, there is little spread in the total adsorption energy u_i .

Between those extremes, near the pzc, w will have a maximum. If w is not constant, it can be derived that, with N_i constant,

$$du_i = df + \left(\left(\frac{u_i - f}{w} \right)^2 - 1 \right) \times \frac{w}{u_i - f} dw. \quad [22]$$

The corrections to [12] will be positive for some sites (for $du > 0$, if $u_i - f > w > 0$ or $0 > u_i - f > -w$), negative for other

sites (if $u_i - f < -w < 0$ or $0 < u_i - f < w$). On introducing [12] into [14] errors are introduced which will tend to cancel on carrying out the integration.

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