

The ZnO/aqueous solution interface II. Mechanism of the slow process

Citation for published version (APA):

Trimbos, H. F. A., & Stein, H. N. (1980). The ZnO/aqueous solution interface II. Mechanism of the slow process. *Journal of Colloid and Interface Science*, 77(2), 397-406. [https://doi.org/10.1016/0021-9797\(80\)90309-4](https://doi.org/10.1016/0021-9797(80)90309-4)

DOI:

[10.1016/0021-9797\(80\)90309-4](https://doi.org/10.1016/0021-9797(80)90309-4)

Document status and date:

Published: 01/01/1980

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

The ZnO/Aqueous Solution Interface

II. Mechanism of the Slow Process¹

H. F. A. TRIMBOS AND H. N. STEIN

Laboratory of General Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

Received July 31, 1979; accepted December 24, 1979

In addition to adsorption of H^+ and OH^- ions at the ZnO/aqueous solution interface a slow H^+ or OH^- consuming process has been observed. Although the amount of H^+ or OH^- consumed by this process is approximately proportional to the square root of the time, a diffusion-controlled process is excluded. All phenomena observed can be accounted for by the following mechanism: At $pH < 8.9$, H^+ ions react with surface hydroxyl groups, but, after an initial stage, this reaction can proceed only if a free electron is available at or near the reacting group. Similarly, at $pH > 8.9$, OH^- ions react with $\equiv ZnOH$ groups, but this reaction is, after an initial stage, confined to groups which have a hole (a vacant state in the valency band) in their vicinity. This causes the reaction rate of the slow process to be governed by the development of a space charge in the solid.

INTRODUCTION

Recently (1) an investigation was reported on the discrepancies existing in the literature (2) between the double-layer capacities at the ZnO/aqueous electrolyte solution interface as obtained by three different methods: (a) The theoretical, Gouy-Chapman capacity of the diffuse double layer; (b) the capacity as measured in titration experiments; and (c) the capacity as measured in an ac bridge.

As the main cause for these discrepancies, the lack of taking into account a "slow" process, consuming H^+ or H^- ions, was held responsible. This process is superimposed on the adsorption of these ions at the ZnO surface: by extrapolating the slow process to time = zero, capacities were obtained which agree well both with theoretical capacities and (at the pzc) with capacities

measured at AgI/aqueous solution interfaces (3). Obviously a reliable extrapolation of the slow process requires knowledge of its mechanism. The present paper reports additional experiments, performed in order to elucidate this mechanism.

EXPERIMENTAL

Materials

The same materials were employed as described previously (1). ZnO single crystals were obtained from Prof. Heiland, Technische Hochschule Aachen, West Germany²; they had been grown from the vapor phase. Double-tracered $^{24}Na^{82}Br$ was obtained as described earlier (4).

Apparatus

H^+ and OH^- consumption by the ZnO was studied as described previously (1). Electrophoresis was carried out in a cell according to Smith and Lisse (5) using platinized Pt electrodes. $^{24}Na^{82}Br$ adsorp-

² The authors thank Prof. Heiland for placing these crystals at their disposal.

¹ The contents of this paper have been presented in abstract at the EUCHEM conference on Solid State Chemistry and Electrochemistry, Endorf, West Germany, 1979.

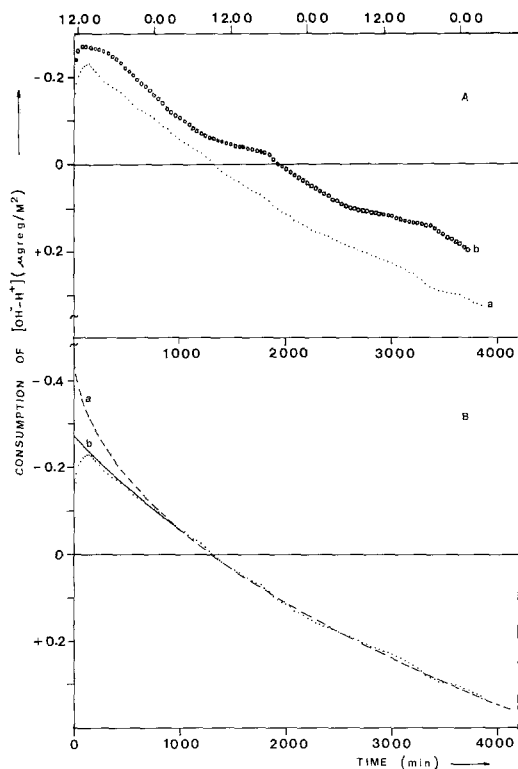


FIG. 1. $[\text{OH}^- - \text{H}^+]$ consumption by ZnO in 0.1 M NaCl solution at pH = 8. (A) Influence of light: (a) in the dark; (b) unprotected against light. (B) Comparison with theory: (a) $\sigma = At^{1/2}$; (b) according to relation [7] (after integration).

tion on ZnO single crystal was performed in an apparatus described earlier (4).

Procedure

(1) Electrophoresis: During the experiments on H^+ or OH^- consumption by a ZnO suspension as a function of time at constant pH (1), at predetermined times 25 ml was pipetted from the suspension. This sample was immediately filtered with suction in an atmosphere of purified nitrogen (about 2 min). To the clear filtrate, 50 μl of the original suspension was added, and the resulting suspension was introduced into the electrophoresis cell. Electrophoretic mobilities were converted into ζ -potentials using the method of Wiersema *et al.* (6), taking into account the mobilities of Na^+ and

Cl^- ($m_+ = 45.6 \Omega \cdot \text{cm}^2 \text{eq}^{-1}$ and $m_- = 68.4 \Omega \cdot \text{cm}^2 \text{eq}^{-1}$). In these calculations the radius of the ZnO particles was taken as the radius of a sphere of specific surface equal to that of the ZnO sample.

(2) $^{24}\text{Na}^{82}\text{Br}$ adsorption was investigated by the same method as described earlier (4) at pH 7.7 and 10.6. The pH was kept constant by means of titration equipment similar to that used for the suspension measurements (1). After contact with the $^{24}\text{Na}^{82}\text{Br}$ solution for 4 hr, the single crystal was washed seven times with untraced NaBr solution, and then etched in 0.01 M HCl. No difference with etching in HClO_4 instead of HCl was noticed.

RESULTS

An overall view of the H^+ and OH^- consumption at constant pH as a function of time has been presented in the preceding paper (1). One experiment is described with additional information (see later) in Fig. 1A and another one in Fig. 2A. Negative ζ -potentials were observed throughout (Fig. 3), even in the suspension at pH 8.0 after 4000 min reaction, when the ZnO has consumed a net amount of H^+ . By reason of charge balance, an additional amount of Cl^- must have been transferred behind the electrokinetic slipping plane.

In fact, the ζ -potentials observed are practically independent of the reaction time (Fig. 3). The general course of the ζ -potentials as a function of pH agrees well with Healy and Jellett's data (7).

At all pH values investigated the "slow" reaction can be described approximately (1) by the equation

$$\sigma = At^{1/2} \quad [1]$$

with σ = the amount of H^+ and OH^- consumed by the slow process up to time t .

Figure 4 shows the coefficient A observed as a function of pH; a positive value corresponds with H^+ consumption, a negative one with OH^- consumption. Values of A were determined by least-squares analysis

of the data; values obtained at $[\text{NaCl}] = 0.001 \text{ M}$ are more uncertain because it was more difficult in these solutions to keep the pH constant as compared with 0.1 and 0.01 M solutions.

In Figs. 1A and 2A, two experiments are shown: one (a) in a reaction vessel shielded against light influence, the other (b) not protected against light. The latter curve shows the diurnal rhythm of light and dark: light enhances OH^- consumption and counteracts H^+ consumption. This effect was, to the accuracy obtained, independent of the pH and no sign of saturation was found during a 3 day and night experiment.

Figures 5 and 6 show the results of $^{24}\text{Na}^+$ and $^{82}\text{Br}^-$ adsorption experiments. It is seen that at pH 7.7, Br^- is preferentially adsorbed (which is seen in the bending off of the Br^- activity curve from a straight line

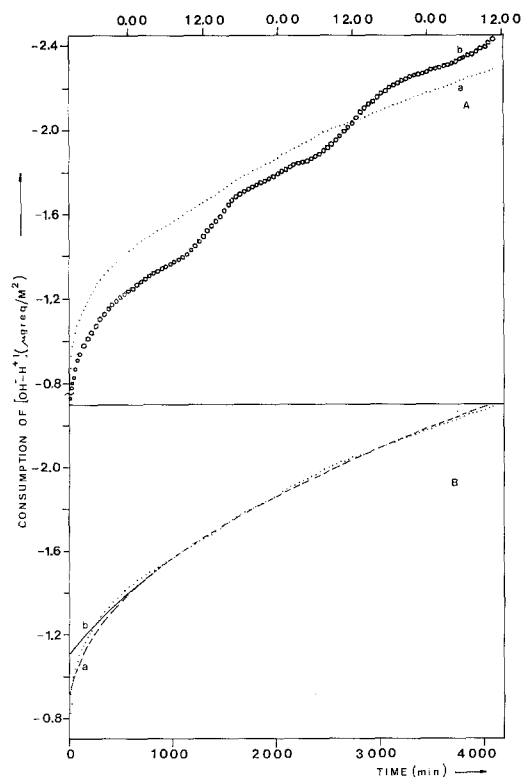


FIG. 2. $[\text{OH}^- - \text{H}^+]$ consumption by ZnO in 0.1 M NaCl solution at pH 10. Symbols as in Fig. 1.

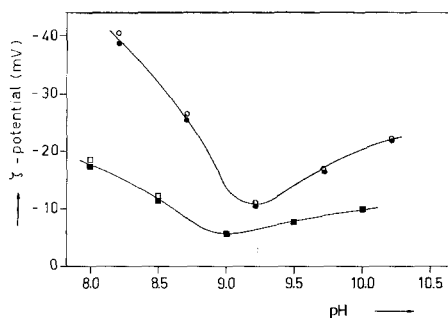


FIG. 3. ζ -potential as a function of pH. ○, After 500 min in 0.001 M NaCl; ●, after 3800 min in 0.001 M NaCl; □, after 500 min in 0.01 M NaCl; ■, after 3800 min in 0.01 M NaCl.

during the later washings) and that even after 4 hr contact with NaBr solution Br^- ions have penetrated far into the ZnO (about 7000 Å). At pH 10.6 similar data hold for the Na^+ ions. Penetration of such ions, however, can for steric reasons be expected only at dislocations.

DISCUSSION

Any mechanism for the slow reaction must be compatible with the following conditions:

- (1) The kinetics of the process can be approximated between 1200 and 4000 min by a relation of the type $\sigma = At^{1/2}$.
- (2) The proportionality constant A depends on the pH.
- (3) A does not depend on the NaCl concentration.
- (4) A shows a smooth transition, without a break in the slope, from positive to negative values near the pzc (pH 8.7); and at equal distances from pH 8.9, the absolute values of A are about equal.
- (5) The ζ -potential is < 0 and independent of the time.
- (6) Light stimulates OH^- consumption and counteracts H^+ consumption.
- (7) At $\text{pH} < 8.9$, Br^- ions from NaBr solution (presumably also Cl^- in NaCl solution) penetrate deep into the ZnO; at $\text{pH} > 8.9$ the same obtains for Na^+ ions.

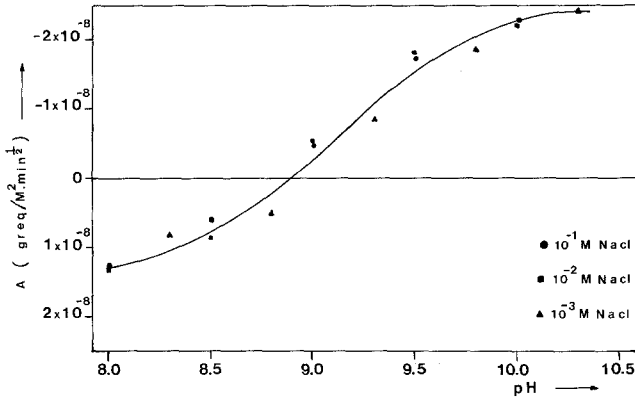


FIG. 4. Proportionality constant (A) from $\sigma = At^{1/2}$ as a function of pH.

A $t^{1/2}$ proportionality often indicates a diffusion-controlled process; thus we checked this possibility carefully. Since the suspension was intensively stirred, concen-

tration gradients in the liquid phase may be excluded. Moreover, conditions in the liquid medium remain constant with time except for a small increase in electrolyte

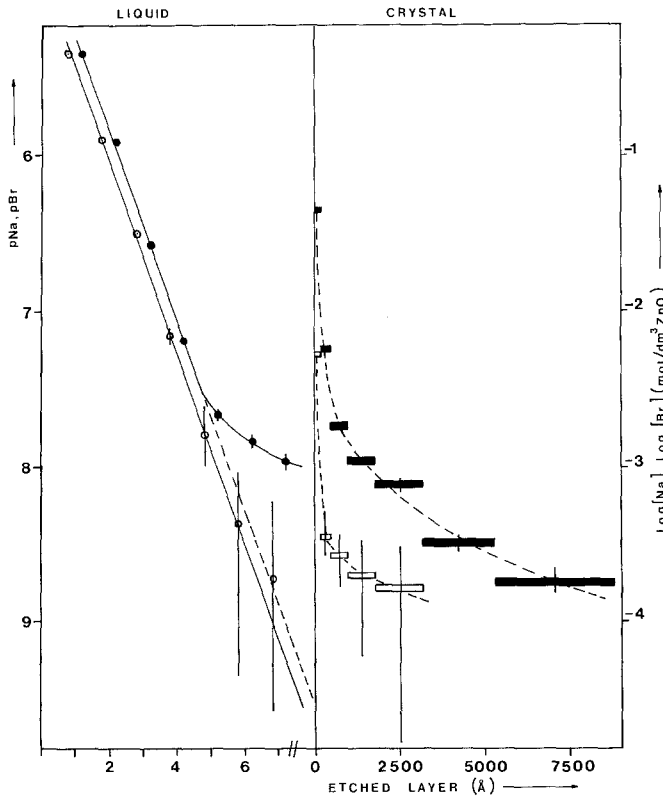


FIG. 5. Radioactive tracer adsorption and penetration in $1.4 \times 10^{-3} \text{ M Na}^{24}\text{Br}^{82}$ at pH 7.7. ●, Concentration of Br in wash fractions; ○, concentration of Na in wash fractions; ■, concentration of Br in crystal, calculated from etch fractions; □, concentration of Na in crystal. The vertical lines indicate the probable error of the concentrations, due to errors in the tracer "count" procedure.

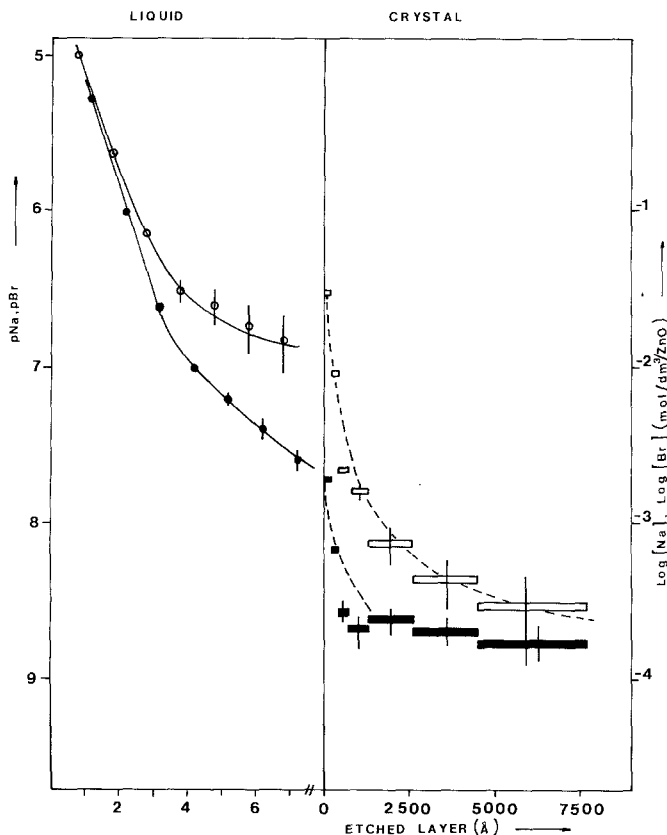


FIG. 6. Radioactive tracer adsorption and penetration in $1.5 \times 10^{-3} M$ $\text{Na}^{24}\text{Br}^{82}$ at pH 10.6. Symbols as in Fig. 5.

concentration due to the addition of NaOH or HCl to keep the pH constant. Diffusing species in the solid might be H^+ at $\text{pH} < 8.9$ and OH^- at $\text{pH} > 8.9$. To be sure, H^+ ions should have a much higher diffusivity in ZnO than OH^- which would lead to a contradiction with condition 4. This, however, might be circumvented by postulating OH groups in the bulk of the initial ZnO at point defects; at $\text{pH} > 8.9$, the protons of such groups could diffuse out of the ZnO. Diffusion of protons into Fe_2O_3 has been assumed by Onoda and de Bruyn (8). The objection that an accumulation of charge in the solid by such a process would be at variance with condition 5, might be answered by assuming simultaneous transfer of counterions (Cl^- or Na^+ at pH smaller or larger than 8.9, respectively) to the region

behind the electrokinetic slipping plane. However, such a diffusion is influenced by the electric potential generated, such as to superimpose a drift current upon a diffusion current (9):

$$J_{\text{H}^+} = -D \text{grad} [\text{H}^+] - [\text{H}^+] \times \frac{e_0 D}{kT} \text{grad} \psi \quad [2]$$

where

- D = the diffusion constant of protons in ZnO;
- e_0 = the charge of the proton;
- ψ = the local electrical potential;
- J_{H^+} = the flux of H^+ ions.

A $t^{1/2}$ proportionality is obtained only if the second term is negligible compared with

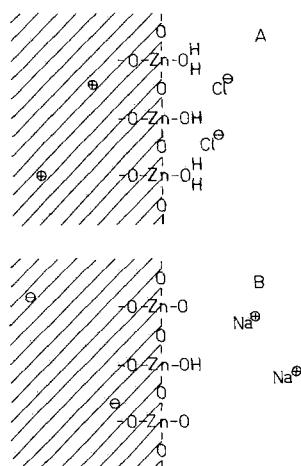


FIG. 7. Schematic representation of the distribution of charges due to the slow reaction: (A) at pH < 8.9; (B) at pH > 8.9.

the first over the entire period during which this relation is observed. If the counterions remain outside the solid (or penetrate the solid only at dislocations), whereas H⁺ diffuse into and out of undisturbed regions of ZnO, we know grad ψ at the boundaries of these undisturbed regions: by Poisson's relation, for a flat surface

$$\frac{d\psi}{dx} = - \int_0^{\infty} \frac{\rho}{\epsilon_r \epsilon_0} dx = - \frac{\sigma}{\epsilon_r \epsilon_0} \quad [3]$$

with

- ρ = space charge density;
- x = distance from the surface, regarded as positive in the direction into the solid;
- $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$;
- ϵ_r = the dielectric constant of ZnO (=8.5 (10)), regarded as independent of x .

In the present context, this relation is applied in the solid. σ is then the total charge per unit surface in the solid if to $d\psi/dx$ is attached its value just behind the phase boundary, but still within the solid.

Thus, after 3800 min at pH 8, where the $t^{1/2}$ relationship is still obeyed, grad ψ would become $\approx 1 \cdot 10^9 \text{ V m}^{-1}$, and if diffusion of protons is rate determining, $d \ln [H^+]/dx$ in the solid must be large compared with $4 \cdot 10^{10} \text{ m}^{-1}$. This, however,

would mean that the proton concentration in ZnO decreases to $1/e$ of its surface concentration well within one unit cell, which excludes a diffusion controlled process.

In view of the order of magnitude of grad $e_0\psi/kT$, the consideration that the double layer near a dislocation is not really flat does not impair our conclusion.

Simultaneous diffusion of equimolar quantities of H⁺ and Cl⁻ into the ZnO at pH < 8.9, or exchange of Na⁺ against H⁺ at pH > 8.9, would remove this discrepancy. In order to be sterically possible, such a process should be restricted to dislocations. However, this mechanism is incompatible with conditions 3 and 4. Moreover, it does not obviously explain condition 6. A mechanism which is consistent with all conditions mentioned is the following:

At the first contact of ZnO with an aqueous solution, adsorption of H⁺ and OH⁻ occurs (indicated as "primary adsorption"). This is saturated at a relatively low degree of surface coverage. In addition, a reaction of surface $\equiv\text{Zn}-\text{OH}$ groups takes place with H⁺ ions at pH < 8.9, with OH⁻ ions at pH > 8.9; the rate of this reaction is proportional to the concentrations of free electrons or holes (vacant states in the valency band), respectively, at the surface. The charge, transferred by this process to the solid, does not remain at the surface itself but is distributed by electron transport, over the near surface region of the solid, forming a depletion layer or counteracting an accumulation layer at pH < 8.9, forming or enhancing an accumulation layer at pH > 8.9 (see Fig. 7). In Fig. 7 only the charges due to the slow process are indicated; in addition, surface charges are generated by primary adsorption and by chemisorption of Cl⁻.

This mechanism is consistent with conditions 2, 3, and 5, and also with the anti-symmetrical character of the reaction rate with respect to the pzc (condition 4), since it does not involve transport of Na⁺ or Cl⁻ ions in the solid (except in dislocations,

and then not as a rate-determining step). Consistency with condition 1 can be obtained as follows: Proportionality of the reaction rate with the free electron concentration near the surface requires a proportionality with $\exp y_s$ (where $y_s = e_0 \psi_{\text{solid}}/kT$, ψ_{solid} = the potential difference between the surface and the bulk solid, and $-e_0 \psi_{\text{solid}}$ is called "band bending" by solid state chemists (11)³). Similarly, proportionality with the hole concentration requires a proportionality with $\exp(-y_s)$. The sign of y_s is chosen in agreement with solid state usage, taking the potential in the bulk solid as zero. dy/dx at the surface is known from the experimental data through relation [3], insofar as it is due to the slow process (in other words, $(dy/dx)_{x=0}$ is divided into a part due to primary adsorption and chemisorption of Cl^- and a part due to the slow process; the additivity of both parts of $(dy/dx)_{x=0}$ follows from the additivity of the charges σ transferred to the solid by the corresponding processes, cf. [3]). According to Dewald (12) for a flat space charge in an n-type semiconductor,

$$\left(\frac{dy}{dx}\right)_{x=0} = \mp \left(\frac{2e_0^2 N_D}{\epsilon_r \epsilon_0 kT}\right)^{1/2} (fe^{y_s} - f - y_s + \ln [f + (1-f)e^{y_s}])^{1/2} \quad [4]$$

with

N_D = donor concentration in the ZnO, assumed to be independent of x ;

f = degree of dissociation of these donors in the bulk ZnO.

The minus sign is for $y_s > 0$ and the + sign is for $y_s < 0$.

Thus, for the slow process by reason of the additivity of the two contributions to $(dy/dx)_{x=0}$:

$$\left(\frac{dy}{dx}\right)_{x=0} = \mp \left(\frac{2e_0^2 N_D}{\epsilon_r \epsilon_0 kT}\right)^{1/2} \{ (fe^{y_s} - f - y_s + \ln [f + (1-f)e^{y_s}])^{1/2} - (fe^{y_0} - f - y_0 + \ln [f + (1-f)e^{y_0}])^{1/2} \} \quad [5]$$

³ The ZnO is treated, throughout this paper, as a non-degenerated semiconductor.

TABLE I

Values for y_0 , Calculated for $f = 0.5$ and $N_D = 10^{25} \text{ m}^{-3}$

pH	$10^{-3} M \text{ NaCl}$ (y_0)	$10^{-2} M \text{ NaCl}$ (y_0)	$10^{-1} M \text{ NaCl}$ (y_0)
8.0	—	9.29	9.24
8.3	8.34	—	—
8.5	—	8.36	7.73
8.8	5.88	—	—
9.0	—	5.15	4.99
9.3	6.16	—	—
9.5	—	7.70	7.60
9.8	7.75	—	—
10.0	—	8.10	8.16
10.3	8.28	—	—

where y_0 is the reduced surface potential in the solid due to primary adsorption and chemisorption of Cl^- ions.

At chosen values of f and N_D , y_0 can be adjusted such as to let $(dy/dx)_{x=0}$ due to the slow process approximate, say at $1200 \text{ min} < t < 4000 \text{ min}$, to a $t^{1/2}$ proportionality (which means that, at $\text{pH} < 8.9$, $e^{+y_s} t^{1/2}$ must be nearly independent of time; at $\text{pH} > 8.9$ $e^{-y_s} t^{1/2}$ must be nearly independent of time; since $\sigma = At^{1/2}$ requires $d\sigma/dt = A/(2t^{1/2})$, and this latter quantity should be proportional to e^{y_s} or e^{-y_s} , respectively).

Table I presents some data, calculated for $f = 0.5$ and $N_D = 10^{25} \text{ m}^{-3}$. Other values for f and N_D will lead to different y_0 values; however, the $\sigma(t)$ curves calculated from the different sets of parameters (see below) differ from each other only to extents negligible in comparison with the experimental accuracy of the data.

From relation [5], the charge transferred to the solid by the slow reaction at any time can be calculated. In order to do this, we write:

$$\frac{d\sigma}{dt} = \frac{d\sigma}{dy_s} \frac{dy_s}{dt} = B e^{y_s} \quad \text{at } \text{pH} < 8.9;$$

$$= B e^{-y_s} \quad \text{at } \text{pH} > 8.9. \quad [6]$$

Here B can be calculated from $d\sigma/dt$ at one particular time (say 1200 min), at which y_s is known from the fitting procedure. Thus:

$$dt = \frac{1}{B} e^{\mp y_s} \frac{d\sigma}{dy_s} dy_s = \frac{1}{B} e^{\mp y_s} \frac{fe^{y_s} - 1 + (e^{y_s} - fe^{y_s})/(f + e^{y_s} - fe^{y_s})}{2(fe^{y_s} - f - y_s + \ln [f + e^{y_s} - fe^{y_s}])^{1/2}} dy_s \quad [7]$$

Here the minus sign refers to $\text{pH} < 8.9$ and the plus sign to $\text{pH} > 8.9$.

By integrating [7] from y_s at 1200 min to a value y'_s , the time at which y'_s is valid can be calculated. By combining the result [3] and [5], $\sigma(t)$ is evaluated.

The Figs. 1 and 2 compare the $\sigma(t)$ thus calculated with the experimental data and with $\sigma = At^{1/2}$. The "space charge" mechanism is seen to describe the experimental data over a more extended time period than the $t^{1/2}$ relation.

From the calculations, a value for y'_s and for σ at $t = 0$ are found. At that time, y'_s differs from y_0 , because the $\sigma(t)$ calculations are based on the assumption that primary adsorption and chemisorption, giving y_0 its value as required for the descrip-

tion of the slow process, proceed instantaneously.

In reality, these processes require some time, and the kinetics of the slow reaction cannot be expected to follow the calculated $\sigma(t)$ relation from $t = 0$ on, but only after some time during which changes in y_s are caused not only by the slow reaction, but by the other reactions as well.

The charge ω_0 transferred at any pH by primary adsorption and chemisorption to the ZnO can be calculated from y_0 . The values are plotted, as a function of pH, in Fig. 8. They are negative at all pH values, since all y_0 values are positive (see Table I). This can be understood by the following mechanisms:

(a) At $\text{pH} < 8.9$: On the first contact of

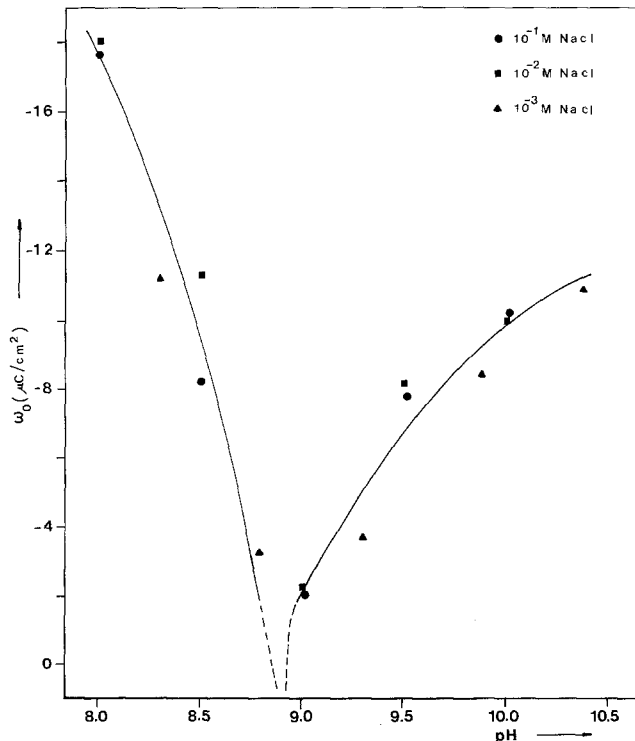


FIG. 8. The surface charge in the solid (caused by primary adsorption of H^+ or OH^- and by chemisorption) as a function of pH.

ZnO with the aqueous solution, adsorption of H^+ on $\equiv ZnOH$ groups and chemisorption of Cl^- on $\equiv Zn$ ions near the surface take place. Of the charges transferred to the ZnO by these processes, the negative charges imparted by Cl^- chemisorption are mobile (ZnO is an electronic semiconductor) and distribute themselves over the surface region (Fig. 9A).

(b) At $pH > 8.9$: On the first contact with ZnO with the aqueous solution, $\equiv ZnOH$ groups combine with OH^- ions forming $\equiv ZnO^-$; again the negative charge imparted by this process to the ZnO forms a space charge region (Fig. 9B).

In terms of solid state chemistry, $\equiv ZnCl^{(-)}$ and $\equiv ZnO^{(-)}$ groups form surface states whose energy levels should be situated as depicted in Fig. 10 at A and B, respectively. As far as the present authors are aware, no independent data are available about the energy levels of such states at the ZnO/aqueous solution interface; the most direct indication is the value of 1.1–1.7 eV for ΔE (see Fig. 10) for a surface state connected with adsorbed Cl^- ions at the interface ZnO/dilute gas (13). The level of a $\equiv Zn-O^{(-)}$ group may be supposed to be well above E'_v (cf. Ref. (14)). Both data are quite well compatible with a situation

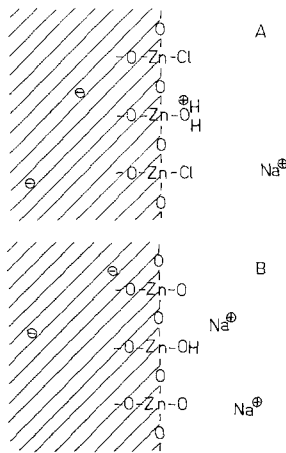


FIG. 9. Schematic representation of the charges transferred to the ZnO by primary adsorption and chemisorption: (A) at $pH < 8.9$; (B) at $pH > 8.9$.

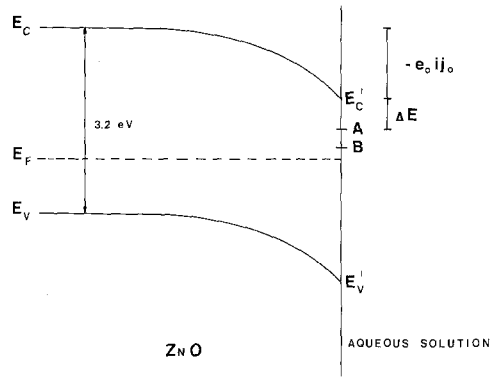


FIG. 10. Situation of energy levels (schematic): E_c , lower edge of conduction band in the bulk ZnO; E'_c , the same at the surface; E_v , upper edge of valence band in the bulk ZnO; E'_v , the same at the surface; E_f , Fermi level.

of levels A and B above the Fermi level E_f , as is necessary in order to enable the surface states concerned to yield an electron as required by the positive y_0 values found.

Thus, in all cases an accumulation layer is formed at the surface of the ZnO, and in spite of the free electrons at $pH < 8.9$ at the surface being consumed by the reaction with H^+ , there remains an accumulation layer throughout the period investigated. The process, depicted schematically in Fig. 7A, is thus superimposed on an accumulation layer caused by chemisorption of Cl^- .

This conclusion is supported by two experimental facts:

(a) The net negative charge behind the electrokinetic slipping plane even at $pH < pH_{pzc}$ (Fig. 3);

(b) The influence of light (Figs. 1A and 2A): light stimulates the dissociation of donors in ZnO, forming additional free electrons and holes; however, since the product of the free electron and hole concentrations must remain constant (15), the surplus electrons have to be carried away from the surface and therefore in a ZnO with an accumulation layer the surface electron concentration will be reduced by light, whereas the surface hole concentration is increased.

The surface charge due to the slow process calculated from y_0 and y_s at $t = 1200$

min by relation [5], can be added to the amount of OH^- consumed by the ZnO up to that time to give a surface charge due to both primary adsorption of H^+ and OH^- and chemisorption of Cl^- . This surface charge is referred to an arbitrary initial charge present on the ZnO as added.

In this way, the same value for σ_0 is found as by extrapolating the $\sigma = At^{1/2}$ relation to $t = 0$ (see Ref. (1), Fig. 2). On the other hand a value of the total charge in the space charge layer in a situation where the reduced surface potential in the solid is $y_0(\omega_0)$ can be calculated from relation [4] (see Fig. 8). The trend of σ_0 as a function of pH differs, especially at $\text{pH} < 8.9$, from that of ω_0 . This difference is attributed to chemisorption of Cl^- . The maximum surface charge ω_0 ($0.18 \times 10^{-6} \text{ C cm}^{-2}$) corresponds to about 1% of a monolayer of Cl^- , thus the charge due to primary adsorption of Cl^- can easily be accommodated in a monolayer.

The σ_0 values calculated by this extrapolation method are subject to some uncertainty, insofar as the period at the beginning during which primary adsorption, chemisorption of anions, and the slow process take place simultaneously cannot be elucidated on the basis of the data available at present. In this respect measurements of the chemisorption of anions might prove helpful.

It may be surprising that y_0 is relatively large in the vicinity of the pzc. However, it should be borne in mind that y_0 refers to a potential gradient in the solid, whereas the pzc refers to the condition that equal amounts of potential determining ions (H^+ and OH^-) are taken up by the solid. The latter condition is easily compatible with a nonzero value of y_0 .

CONCLUSION

The data available on the slow consumption of H^+ and OH^- ions by ZnO can be explained by a mechanism comprising reactions with surface $\equiv\text{ZnOH}$ groups with a free electron or hole, respectively.

ACKNOWLEDGMENTS

This work has been carried out under auspices of the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (Z.W.O.). The authors thank in addition Dr. W. Smit and Mr. A. J. G. van Diemen for many helpful discussions.

REFERENCES

1. Trimbos, H. F. A., and Stein, H. N., *J. Colloid Interface Sci.* **77**, 386 (1980).
2. Blok, L., Ph.D. Thesis, Utrecht, 1968.
3. Lyklema, J., Ph.D. Thesis, Utrecht, 1957; Lyklema, J., and Overbeek, J. Th. G., *J. Colloid Interface Science* **16**, 595 (1961).
4. Smit, W., Holten, C. L. M., Stein, H. N., de Goey, J. J. M., and Theelen, H. M. J., *J. Colloid Interface Sci.* **63**, 120 (1978).
5. Smith, M. E., and Lisse, M. W., *J. Phys. Chem.* **40**, 399 (1936).
6. Wiersema, P. H., Loeb, A. L., and Overbeek, J. Th. G., *J. Colloid Interface Sci.* **22**, 78 (1966).
7. Healy, T. W., and Jellett, V. R., *J. Colloid Interface Sci.* **24**, 41 (1967).
8. Onoda, G. Y., Jr., and de Bruyn, P. L., *Surface Sci.* **4**, 48 (1966).
9. Many, A., Goldstein, Y., and Grover, N. B., "Semiconductor Surfaces," p. 79. North Holland, Amsterdam, 1971.
10. Heiland, G., Mollwo, E., and Stöckmann, F., *Solid State Phys.* **8**, 191 (1959).
11. Many, A., Goldstein, Y., and Grover, N. B., "Semiconductor Surfaces," p. 347. North Holland, Amsterdam, 1971.
12. Dewald, J. F., *Bell Syst. Techn. J.* **39**, 615 (1960).
13. Levine, J. D., Willis, A., Bottoms, W. R., and Mark, P., *Surface Sci.* **29**, 144 (1972).
14. Morrison, S. R., *Surface Sci.* **50**, 329 (1975).
15. Many, A., Goldstein, Y., and Grover, N. B., "Semiconductor Surfaces," p. 57. North Holland, Amsterdam, 1971.