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**Citation for published version (APA):**

Smit, W., Holten, C. L. M., Stein, H. N., de Goeij, J. J. M., & Theelen, H. M. J. (1978). A radiotracer determination of the sorption of sodium ions by microporous silica films. *Journal of Colloid and Interface Science*, 67(3), 397-407. [https://doi.org/10.1016/0021-9797\(78\)90228-X](https://doi.org/10.1016/0021-9797(78)90228-X)

**DOI:**

[10.1016/0021-9797\(78\)90228-X](https://doi.org/10.1016/0021-9797(78)90228-X)

**Document status and date:**

Published: 01/01/1978

**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.
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# A Radiotracer Determination of the Sorption of Sodium Ions by Microporous Silica Films

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Received November 4, 1977; accepted April 5, 1978

The sorption of sodium ions from a slightly alkaline solution by microporous silica films of 0.4- to 1.0- $\mu\text{m}$  thickness, obtained on the surface of vitreous silica rods by the hydrolysis of  $\text{SiCl}_4$ , was followed by a  $^{24}\text{Na}^{82}\text{Br}$  double-tracer technique involving the stepwise dissolution of the films with hydrofluoric acid and the analysis of the fractions obtained. The sorption of sodium ions is not restricted to a narrow surface layer near the silica-film/electrolyte-solution interface but extends over the entire depth of the film. Bromide ions are not sorbed to a measurable extent. The concentration profiles of sodium ions found can be interpreted in terms of an interdiffusion of sodium and hydrogen ions. The estimated values of the individual diffusion constants are  $D_{\text{H}^+.\text{free}} = 10^{-15}$  to  $10^{-13}$   $\text{m}^2 \text{sec}^{-1}$  and  $D_{\text{Na}^+} = 10^{-19}$  to  $10^{-14}$   $\text{m}^2 \text{sec}^{-1}$ .

## INTRODUCTION

In a previous paper (1) we investigated the sorption of sodium ions on vitreous silica by a  $^{24}\text{Na}^{82}\text{Br}$  double-tracer technique involving a layerwise dissolution with hydrofluoric acid. The aim of that investigation was to verify whether the porous double-layer (2) and gel-layer concepts (3) can be adequately applied to surfaces of nonporous silica in contact with aqueous solutions. We concluded that after 28 hr of immersion at room temperature no substantial gel layer ( $>0.3$  nm) is formed on this material and thus that the site-binding model (4) is more appropriate for describing the experimental surface-charge densities and zeta potentials in dependence on pH.

The gel-layer concept, however, was introduced by Lyklema (2) in order to account for the high surface charges found by titration of porous silica (5). Perram *et al.* (3) considered their model only of relevance to those systems for which high charges have been reported. In both mathematical models the penetration depth of counterions is

limited. Lyklema (2) introduced a distance parameter (of the order of 1 nm) over which the porosity is supposed to decay to  $e^{-1}$  times its value at the surface. Perram *et al.* (3c) could account quantitatively for both the surface charge and zeta potential data of several oxides by characterizing the interface by a gel layer of thickness 2 to 4 nm, using adsorption potential and dissociation constant values taken from the literature.

Yates and Healy (6) examined the same type of silica as that used by Tadros and Lyklema (5), viz., BDH-“precipitated” silica, by several techniques. The OH density, as determined by tritium exchange, is according to these authors consistent with a gel layer of hydrolyzed material with a thickness of at least 1.2 nm. However, these authors also concluded that special conditions are required to form this gel layer. Recently, Grigorovich *et al.* (7) studied silica films, deposited on the surface of silicon prisms by the hydrolysis of  $\text{SiCl}_4$ , using the method of multiattenuated total

internal reflection infrared spectroscopy. The films have a homogeneous, microporous structure with pore sizes close to the size of water molecules. Silanol groups in these micropores undergo fast deuterio exchange and are the adsorption sites for physisorbed water. If this is true, we should expect that microporous silicas sorb sodium ions not only in a superficial layer but throughout the material. The aim of the present paper is to test this hypothesis.

#### EXPERIMENTAL

*Silica films.* The silica films were deposited at room temperature on sets of five pieces of vitreous silica with a circular diameter of 2 mm and length of 8 cm, which were clamped in a PTFE holder. After the silica surfaces were cleaned with 5% aqueous hydrofluoric acid solution, the rods were degreased in condensing vapor of carbon tetrachloride and flamed in a colorless Bunsen burner flame. Five or six sets of rods were coated simultaneously. The sets were mounted (free ends pointing downward) on the bottom of a rotating (100 rpm) PTFE disk in a tube, with the disk situated near the top of the tube. At the lower, closed end of this tube, two flows of nitrogen were mixed, the one passing through a drying column and an ampule with silicon tetrachloride (BDH) successively and the other through a gas wash bottle with deionized water. After the tube was flushed with the wet nitrogen, the  $\text{SiCl}_4$  vapor was allowed to enter the tube for about 1 hr, after which the flushing with wet nitrogen was continued for about 30 min. One of the sets was used for checking whether the total amount of silica deposited was sufficient; the amounts of silica on the other sets were determined as part of the sorption measurements.

To correlate the amounts of silica dissolved during etching with penetration depth, a rod with a polished flat plane over the entire length was coated simultaneously

with the sets of rods. Parts of the plane were masked by self-adhesive tape in order to obtain sharp edges between substrate and deposit. The thickness of the deposit was measured by a Talystep apparatus (Rank Precision Industries Ltd.). The thickness found for a layer of  $130 \mu\text{g}$  of  $\text{SiO}_2/\text{cm}^2$  of geometrical macroscopical surface was about  $0.9 \mu\text{m}$ . Thus,  $1 \mu\text{g}$  of  $\text{SiO}_2/\text{cm}^2$  found in the etching experiments is equivalent to 7 nm of thickness.

The silica films were washed free from HCl by immersing the sets of rods for at least 2 days in tubes filled with distilled water which was renewed three times. After removal from the wash solution the rods were freed from the adhering water layer by drying above silica gel. Hereafter, the rods were brought into equilibrium with water in a jar with a layer of water at the bottom. Various washed silica films, taken at random during the procedure, were analyzed for chlorine by neutron activation analysis. The average for nine films amounted to  $(3.9 \pm 1.1) \times 10^{-2}\%$  by weight.

*Zeta-potential measurements* were performed on rods with silica deposits by the method described earlier (8).

*Surface area measurements by nitrogen adsorption* were performed with an Area-meter (Ströhlein & Co.). As sample we used 30 vitreous silica rods of 8-cm length covered by a silica film. The total geometrical macroscopic surface area of the film was  $130 \text{ cm}^2$ . The volume of the sample was compensated by the same number of uncovered vitreous silica rods in the reference vessel. The samples were outgassed at  $105^\circ\text{C}$  for 22 hr in a stream of dried nitrogen at reduced pressure (7 mm Hg), prior to nitrogen adsorption. The nitrogen adsorption was repeated after outgassing at 160 and  $200^\circ\text{C}$ . The amount of silica deposited on the rods was determined by dissolution of the film in HF solution. The surface area measurements were repeated on fresh coatings.

*Surface area measurements* were also performed by the method of negative adsorption (9–11). In this method  $\text{Br}^-$  ions can be used because they are not specifically adsorbed on or absorbed in the silica film (see below). Before the actual sorption experiment a set of rods was rotated in 3.00 ml of  $5 \times 10^{-6} M$  double-tracered neutral  $^{24}\text{Na}^{82}\text{Br}$  solution (solution 0) in a polypropylene tube for 15 min (immersion depth of the rods, 53 mm). Then the set of rods with an adhering liquid layer was transferred to a tube with 3.5 ml of water in which it is rotated for 10 min (solution W). The weight  $m_0$  of the adhering liquid layer followed from the weight loss of solution 0. The specific  $^{24}\text{Na}$  and  $^{82}\text{Br}$  activities as well as the conditions of measurements were the same as those described earlier (1).

The surface  $S$  ( $\text{cm}^2$ ) of the immersed parts of the silica film was calculated with the relation

$$S \cdot \sigma_a^- = (m_0 A_0 - A_w) \cdot f,$$

where  $\sigma_a^-$  is the surface charge ( $\text{C cm}^{-2}$ ) corresponding to the deficit of  $\text{Br}^-$  ions in the diffuse part of the double layer (calculated from the  $\zeta$  potential, see later),  $A_w$  is the  $^{82}\text{Br}$  activity (cpm) in solution W,  $A_0$  is the  $^{82}\text{Br}$  radioactive concentration (cpm/g) of solution 0, and  $f$  is the conversion factor of c.p.m. to the charge in C of the corresponding  $\text{Br}^-$  ions. Since  $m_0 A_0$  and  $A_w$  differ only slightly, the precision in the activity measurements was improved by repeated countings.

*Sorption experiments.* After the washing in the surface measurement experiment the set of rods was transferred to a tube containing 2.5 ml of an  $8 \times 10^{-3} M$  double-tracered NaBr solution of about pH 9.6 (solution A). The washing, etching, and counting procedures were mainly as described previously (1). The dissolution rate of the silica film in 1.5 M HF is much faster than that of the vitreous silica substrate (see below).

In preliminary experiments it was already

established that sodium ions penetrate to the end of the silica film. Thereafter, we made it our object to measure concentration profiles after various immersion times in an attempt to estimate the individual diffusion coefficients of the exchanging  $\text{H}^+$  and  $\text{Na}^+$  ions. After four 3-sec washings with 3.5 ml of acetone–water mixture (96:4 w/w), the adhering acetone was allowed to vaporize (about 15 min) and the rods were etched 12 times in 3 ml of 1.5 M HF for periods of 1 or 2 sec at the beginning and increasing to 30 to 45 sec at the end. These etchings reached beyond the precipitated film. The silicon in the etching fractions (and in solutions 0) was determined as before (1). The sodium ion concentration in solution A was determined by flame emission photometric analysis. The pH of solutions A was measured after the immersion of the rods with a microcombination pH probe (MI-410, Microelectrodes, Inc.).

## RESULTS

The zeta potential of the silica film was measured in 0.01 M NaCl in dependence on pH for comparison with the measurements on vitreous silica (1). At the time of measurement of the zeta potential, the rods had been in contact with the solution concerned about 1 hr. The results are shown in Fig. 1. Measurements were also performed in 0.008 M NaBr at pH 9.6. The zeta potentials found after immersion times of 1 hr,  $-51 \pm 4$  mV, and 1 night,  $-54 \pm 4$  mV, do not differ significantly.

Since the zeta potential is required in the surface area measurement, we also performed measurements in neutral (pH 6–7)  $5 \times 10^{-6} M$  NaBr solution. The results of four measurements were in the range  $-40$  to  $-80$  mV, with a mean value of  $-60$  mV. The  $\sigma_a^-$  values were calculated using this mean value with the theory of the flat double layer. From the measured total silicate concentrations in the solutions 0 ( $< 4 \times 10^{-5} M$ ) (using  $\log K_1 = -9.46$  and  $\log K_2 = -12.56$

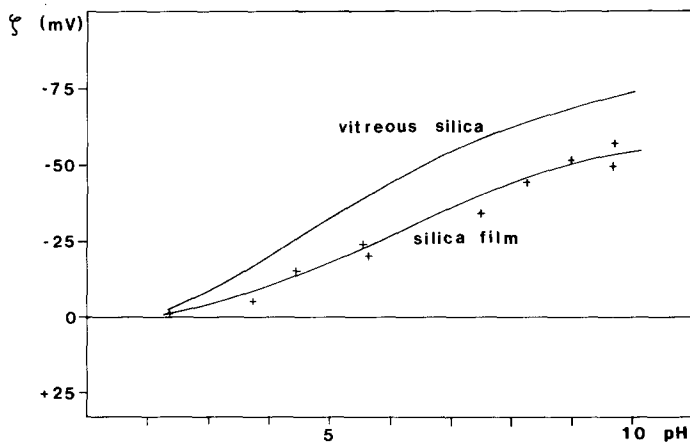


FIG. 1. Variation of zeta potential of silica films with pH;  $10^{-2} M$  NaCl background electrolyte.

(12) and the pH we conclude that the  $\text{SiO}(\text{OH})_3^-$ ,  $\text{SiO}_2(\text{OH})_2^{2-}$ , and  $\text{OH}^-$  concentrations can be neglected in comparison with the  $\text{Br}^-$  concentration. Because of the spread of the zeta potential measure-

ments the probable error in  $\sigma_d^-$  is about 20%. The differences between  $m_0A_0$  and  $A_w$  are much smaller than the values of either  $m_0A_0$  and  $A_w$ . Taking into account the standard deviations of the radioactivity measurements and the possible weight error we estimate the error, of the order of 50 to 100% for the values of  $m_0A_0 - A_w$ . A possible systematic error is an additional sorption of water by the film because of which the weight loss of solution 0 may be something more than the weight  $m_0$  of the adhering liquid layer. The mean of 13 surface area measurements is  $48 \text{ cm}^2$  with a standard deviation of  $45 \text{ cm}^2$ . The geometrical macroscopical surface area of the immersed parts of the silica film was  $16.7 \text{ cm}^2$ .

In the surface area measurements by nitrogen adsorption the pressure difference between sample and reference vessel, read on an oil differential manometer, was about one mm (after outgassing at 105 to  $200^\circ\text{C}$ ). This pressure difference corresponds to a surface area of 10 times the geometrical macroscopic surface area of the film. The mass of the silica films in these measurements was about 5 mg.

In Fig. 2 a typical result of the sorption experiments is shown. In Fig. 2a the count rates of sodium and bromide are plotted versus washing fraction; in Fig. 2b these

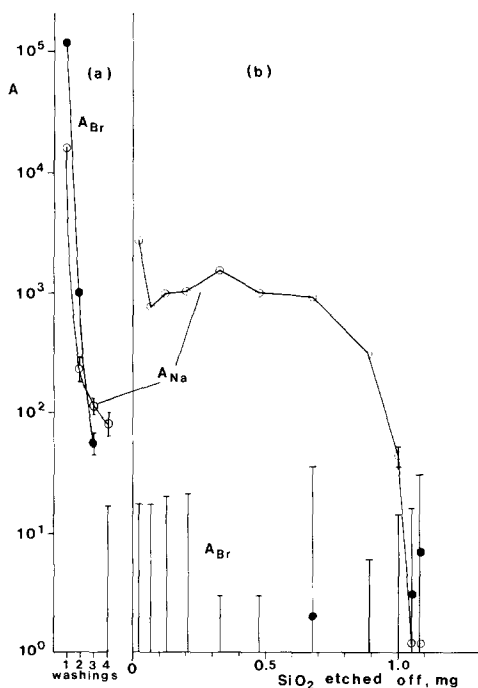


FIG. 2. Typical result of the sorption experiments. Variation of count rate (arbitrary units) with washing fraction (a) and with accumulated silica amounts removed by etching (b) ●,  $A_{\text{Br}}$ ; ○,  $A_{\text{Na}}$ .

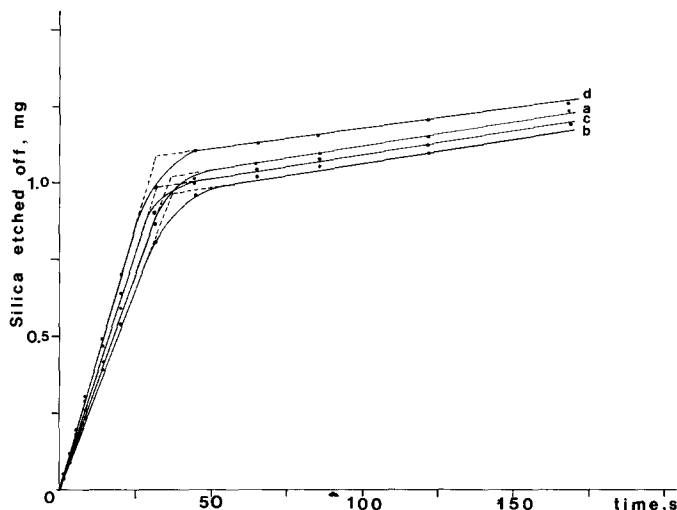


FIG. 3. Cumulative amounts of silica etched off as a function of the accumulated etching times. Silica films of the second series (Table I).

count rates are plotted versus the accumulated silica amounts removed by etching. The bromide activities in the etching fractions were not significantly different from zero in all experiments. The thickness of the silica films could be found by interpolation from plots of the cumulative amounts of silica etched off versus the accumulated etching times, as shown in Fig. 3.

We express the sodium concentration in a layer as the ratio of sodium moles to silica moles in that layer ( $m_{\text{Na}}/m_{\text{SiO}_2}$ ). In the calculation of these concentrations from the sodium count rates and silicon analyses, a correction was applied for the difference between the geometrical surface areas immersed in solution A and in the HF solution. Figure 4 shows the concentration profiles found in the last series of experiments. In Table I relevant data of two series of experiments are collected. The total amount of sorbed sodium also includes the sodium desorbed in the acetone washings, which amounts to only 2 to 3% and was calculated as previously (1).

#### DISCUSSION

The conversion of the charges of the total amounts of sorbed sodium ions (Table I,

fourth column) to surface charge densities depends on the choice of the surface area. The negative adsorption surface area is of

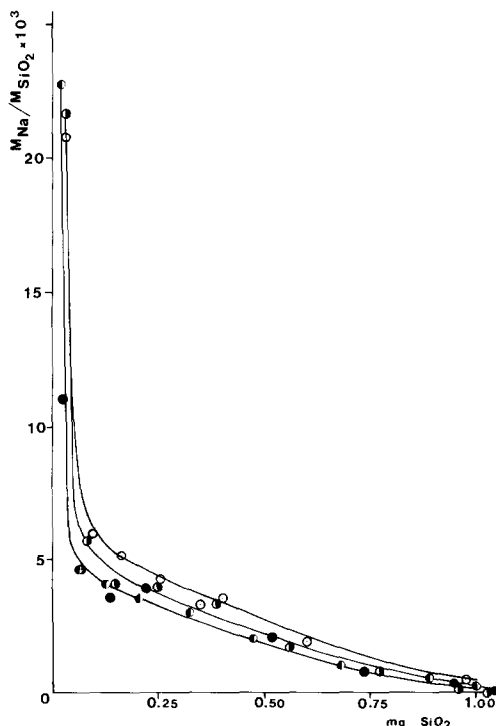


FIG. 4. Concentration profiles, second series of experiments (Table I). ●, a; ◐, b; ◑, c; and ○, d.

TABLE I

Absorption Data of Silica Films in  $7.2 \times 10^{-3} M$  NaBr<sup>a</sup>

Experiment	Immersion time (min)	Thickness ( $\mu\text{m}$ )	Absorbed sodium	
			Total <sup>b</sup> (mC)	Per square centimeter <sup>c</sup> ( $\mu\text{C}/\text{cm}^2$ )
Ia	49	0.84	5.6	33
Ib	117	0.94	6.2	37
Ic	199	0.99	6.6	39
Id	304	0.99	7.8	46
Ie	1063	0.72	7.5	44
IIa	19	0.43	4.1	24
IIb	66	0.41	4.5	26
IIc	177	0.42	5.4	32
IId	300	0.46	5.8	34

<sup>a</sup> Initial pH  $\approx$  9.6; final pH  $\approx$  7.8.<sup>b</sup> Corrected to an immersion depth of 53 mm (16.7 cm<sup>2</sup> of geometrical surface area).<sup>c</sup> Based on a surface area 10 times the geometrical surface area.

the same order of magnitude as the geometrical macroscopic surface area. In fact, the same surface area must be expected because in  $5 \times 10^{-6} M$  NaBr the thickness of the diffuse double layer  $1/\kappa \approx 10^2$  nm, and the surface irregularities of molecular dimensions are not detected by this method. The nitrogen adsorption area, however, is of the order of 10 times the geometrical macroscopic surface area. This difference may be ascribed to pores and surface irregularities. Unfortunately, because of the small amounts of material deposited on the vitreous silica rods, neither a precise surface area determination nor a pore structure analysis can be performed by the nitrogen adsorption method.

Scanning electron micrographs (2100  $\times$  magnification) show a rather smooth surface. This does not exclude, irregularities of molecular dimensions, however. Even when the BET nitrogen surface area is used in the conversion to surface-charge densities, the values found (Table I, last column) are much higher than the surface charge density in the diffuse double layer

$\sigma_d$ , as calculated from the zeta potential and electrolyte concentration. In the present experiments  $\sigma_d$  is about  $1 \mu\text{C cm}^{-2}$ . Since bromide ions are not sorbed to a measurable extent, the charge density  $\sigma_0 = -(\sigma_{\text{Na}}^{\text{ads}} + \sigma_d)$ , required for overall electrical neutrality, must be attributed to the release of protons by silanol groups. This is corroborated by the decrease of the pH. The charge densities  $\sigma_0$  are much higher than the surface-charge densities reported by Bolt (13) and Abendroth (14) for non-porous silicas under comparable conditions.

From the results shown in Figs. 2b and 4 it appears that the sorption of sodium ions, and consequently also the dissociation of silanol groups, is not restricted to a narrow surface layer near the outer silica film/electrolyte solution interface (In this case the HF attack surface area is considered.) Thus, we have to take into account silanol groups at places not immediately attacked by HF.

According to Grigorovich *et al.* (7), the specific surface area of silica films, obtained by the hydrolysis of  $\text{SiCl}_4$  at room temperature, is about  $400 \text{ m}^2 \text{ g}^{-1}$ , as determined from the adsorption of water vapor by the method of piezoelectrical weighing (15). This specific surface area was reproduced very well by them for different conditions for obtaining the films. These films have a homogeneous microporous structure with pore sizes close to the size of the water molecule, i.e., about 0.32 nm. The film evacuated at  $400^\circ\text{C}$  retains its microporous structure. Based on this water specific surface, the surface areas of our films of series I and II are 0.8 and  $0.4 \text{ m}^2$ . If these pores were fully accessible to nitrogen, a significant reading of the order of 20 mm should be observed on the differential manometer of the Areameter instead of the 1 mm found. We conclude that the micropores of the silica films are only for a minor part accessible to nitrogen molecules. Silica with such a behavior has been described earlier (16).

Yates and Healy (6) concluded that physical porosity as assessed by nitrogen adsorption is not necessary for the surface to be porous to ions, because although their BDH-precipitated silica sample was not porous to nitrogen adsorption, the surface charge measured was extremely high. Moreover, Abendroth (17) has shown that transitional pores (diameter, 2–20 nm) lead to lower surface-charge densities. We conclude that the sorption of sodium ions by our silica films is connected with the micropore structure. According to Grigorovich *et al.* (7) the silanol groups in the micropores are the adsorption sites for the water molecules. These silanol groups were detected at the silica film/silicon interface; thus, it is most likely that the silanol groups are dispersed throughout the whole depth of the film.

In the Appendix we treat the sorption of sodium ions as an interdiffusion of  $\text{Na}^+$  (dehydrated) and  $\text{H}^+$ . It is shown that the shape of the experimental concentration profiles can be explained in terms of individual diffusion constants  $D_{\text{H}^+} = 10^{-15}$  to  $10^{-13} \text{ m}^2 \text{ sec}^{-1}$  and  $D_{\text{Na}^+} = 10^{-19}$  to  $10^{-14} \text{ m}^2 \text{ sec}^{-1}$ . Our estimated  $D_{\text{H}^+}$  is several orders of magnitude larger than the  $D_{\text{H}}$  found by Doremus (18) ( $6.4 \times 10^{-23} \text{ m}^2 \text{ sec}^{-1}$  at  $50^\circ\text{C}$ ). However, Doremus'  $D_{\text{H}}$  is an apparent diffusion constant, i.e., treated as if there were no association between  $\text{H}^+$  and  $\equiv\text{SiO}^-$ , whereas our  $D_{\text{H}^+}$  refers to *free*  $\text{H}^+$  ions. It can be shown that  $D_{\text{H}}$  is of the order  $\alpha D_{\text{H}^+}$ , where  $\alpha$  is the degree of dissociation. Moreover, Doremus'  $D_{\text{H}}$  refers to the transition layer of a glass electrode membrane and not to the outer gel layer where the mobility of ions is much higher.

The high "surface"-charge densities, based on the nitrogen adsorption surface area, are an aspect which the silica films have in common with BDH-"precipitated" silica (5, 6). The description "precipitated" suggests that this silica is produced by the following reaction scheme (19, 20): (i) addition of acid to sodium silicate solutions; (ii)

polymerization of the monosilicic and polysilicic acid units to the primary colloidal particles; (iii) growth of these particles with decrease in number in basic solutions in absence of salts; (iv) precipitation of the silica by adding electrolyte or lowering the pH below about 7. The primary particles are according to Carman (21) essentially compact spheres of  $\text{SiO}_2$ , hydrated only at the surface. Such is also the case with silicas obtained by combustion of  $\text{SiCl}_4$ . Such silicas show  $\sigma_0$  vs pH curves (13, 14) which differ little from those obtained for quartz (22) or vitreous silica (1).

BDH-precipitated silica, however, has a relatively small nitrogen BET specific surface area as compared with a normal precipitate and contains at least 10% by weight of physisorbed water (6). This suggests the presence of silanol groups, which are the sorption sites for physisorbed water molecules, not only in a layer of only 1.2 nm thickness, as proposed by Yates and Healy (6), but also in micropores which extend much farther into the bulk, as in our silica films. We expect that BDH-precipitated silica is comparable with a precipitated silica made by a process, covered by a British patent (23), which gives a gel as a mass of granules, each of which is like a sponge containing ultramicroscopic pores.

In our opinion potential-determining ions and counterions can penetrate only the solid side of the interface when silanol groups are intrinsic constituents of the silica and are located in micropores. The penetration depth of counterions will not be restricted to about 2 nm (3c). Perram's (3a) original treatment with  $L = \infty$  must be considered more correct in this respect.

## APPENDIX

### *Estimation of Self-Diffusion Constants*

The absorption of sodium ions by the silica films is accompanied by a release of protons such as follows from the decrease of the pH of the solution. The concentration



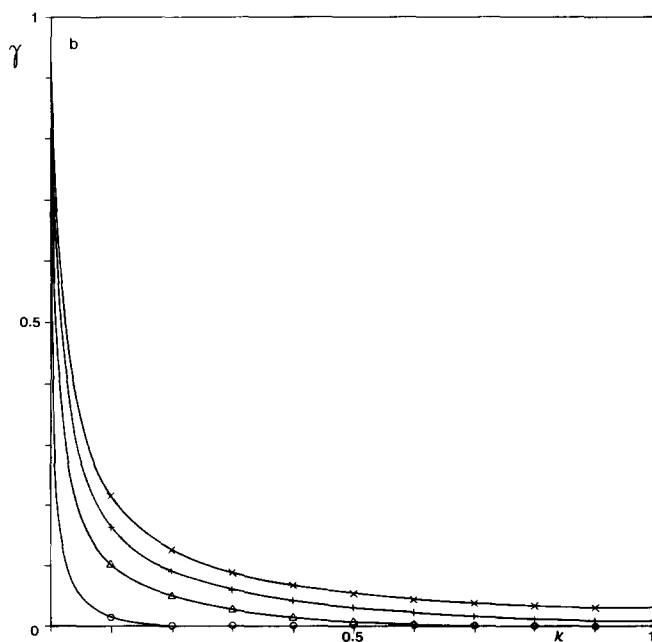
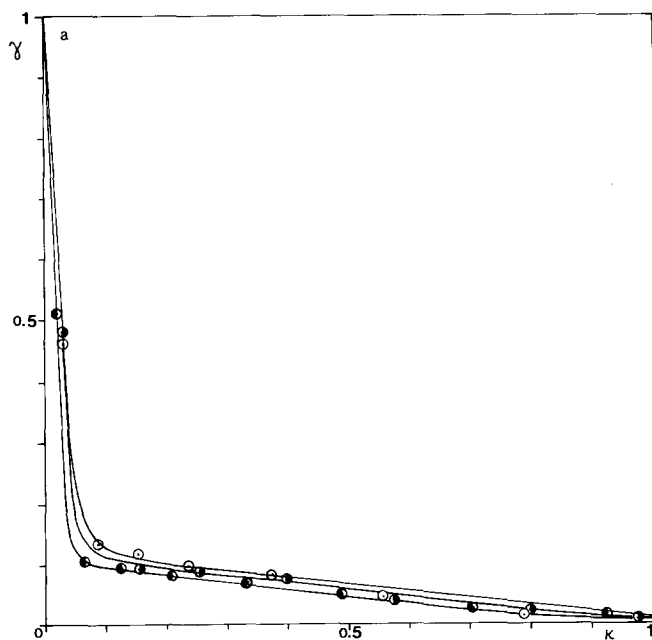


FIG. 5. Normalized concentration profiles. (a) Experimental curves of series II. ●, *b*; ⦿, *c*; ○, *d*. (b) and (c) Theoretical curves, calculated with  $b_1 = 2 \times 10^{-6}$ ,  $b_2 = 10^{-7}$ , and with (b)  $D_B/D_A = 0.0001$  and (c)  $D_A/D_B = 1.00$ . *F* values: ○, 0.01; △, 0.04; +, 0.07, and ×, 0.10.

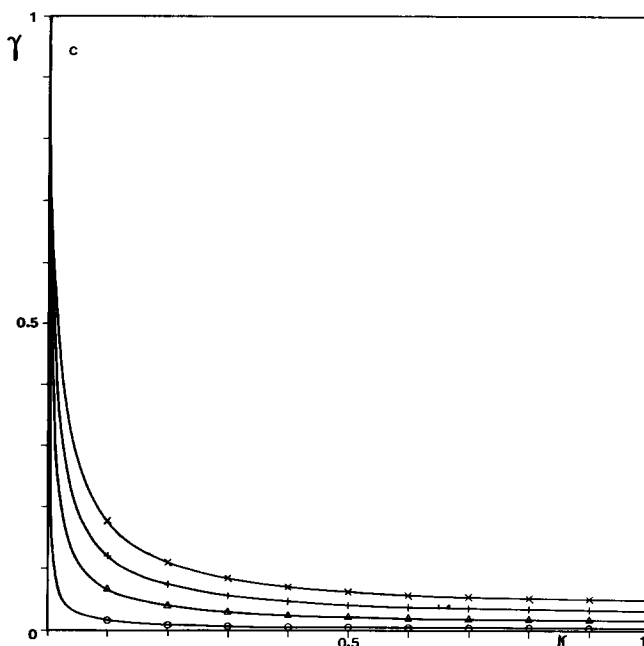
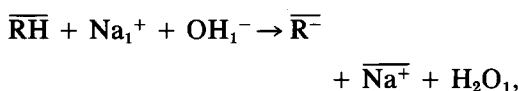


FIG. 5—Continued.

profiles found provide evidence that we are dealing with an interdiffusion of H<sup>+</sup> and Na<sup>+</sup> in the absence of mobile coions (24):



where  $\overline{R}^-$  is  $\equiv SiO^-$ . With the assumptions that coupling effects other than those by electric fields and activity-coefficient gradients are negligible, and with use of the mass action law

$$C_{R^-}C_{H^+}/C_{RH} = K_{RH} = \text{constant}, \quad [1]$$

Helfferich (24) derived the flux equation

$$J_{Na} = -\bar{D} \text{grad } C_{Na}, \quad [2]$$

where the interdiffusion coefficient  $\bar{D}$  is given by

$$\bar{D} = \frac{D_{Na}[A(A - K_{RH}) - C_{Na}(C_{Na} - K_{RH})]}{A(A - K_{RH}) - C_{Na}A(1 - 2D_{Na}/D_H)},$$

$$A \equiv [(C_{Na} - K_{RH})^2 + 4K_{RH}C]^{1/2}. \quad [3]$$

$C \equiv C_{RH} + C_{R^-}$  is the concentration of fixed ionogenic groups (undissociated and dissoci-

ated).  $D_{Na}$  and  $D_H$  are the self-diffusion coefficients of the sodium ions and of the free protons, respectively.

Using the equation of continuity and neglecting  $K_{RH}$  with respect to  $A$ , we arrive at

$$\frac{\partial \gamma}{\partial \tau} = \frac{\partial}{\partial \kappa} \times \left[ \frac{b_1 - \gamma b_2}{(\gamma^2 - 2\gamma b_2 + b_1) - \gamma \frac{\partial \gamma}{\partial \kappa}} \right], \quad [4]$$

$$\times (\gamma^2 - 2\gamma b_2 + b_1)^{1/2} a$$

where  $\tau = D_{Na}t/x_0^2$ ,  $\kappa = x/x_0$ , and

$$\gamma = (C_{Na}/C)/(C_{Na}/C)_{\kappa=0} = (m_{Na}/m_{SiO_2})/(m_{Na}/m_{SiO_2})_{\kappa=0}$$

are dimensionless time, distance, and concentration parameters;  $x_0$  is the thickness of the silica film. The constants  $a$ ,  $b_1$ , and  $b_2$  are given by the relations

$$a = 1 - 2D_{Na}/D_H, \quad b_1 = 4K_{RH}/CR_0^2,$$

$$\text{and } b_2 = K_{RH}/CR_0,$$

where  $R_0 = \beta (m_{Na}/m_{SiO_2})_{\kappa=0}$ ;  $\beta$  is the ratio

TABLE II

Mean Values of  $D_{\text{Na}}$  and  $D_{\text{H}}$  for Different Assumed Values of  $D_{\text{Na}}/D_{\text{H}}$

$D_{\text{Na}}/D_{\text{H}}$	$D_{\text{Na}}$ ( $\text{m}^2 \text{sec}^{-1}$ )	$D_{\text{H}}$ ( $\text{m}^2 \text{sec}^{-1}$ )
$10^{-4}$	$2.1 \times 10^{-18}$	$2.1 \times 10^{-14}$
$10^{-3}$	$1.4 \times 10^{-17}$	$1.4 \times 10^{-14}$
$10^{-2}$	$1.2 \times 10^{-16}$	$1.2 \times 10^{-14}$
$10^{-1}$	$1.1 \times 10^{-15}$	$1.1 \times 10^{-14}$
$10^0$	$1.1 \times 10^{-14}$	$1.1 \times 10^{-14}$

between total silicon atoms and silanol groups in the film.

With Dugger *et al.*'s (25) equilibrium constant of the exchange reaction at the surface ( $\text{p}K = 7$ ) and with  $C_{\text{Na}^+, \text{sol}} = 0,0072 \text{ M}$  and  $\text{pH} \approx 7.8$ , the estimated value of  $(m_{\text{Na}}/m_{\text{SiO}_2})_{\kappa=0}$  is 0.045, a value which is consistent with Fig. 4. The thickness  $x_0$  follows from Fig. 3. The experimental results of Fig. 4 are shown in the normalized form in Fig. 5a.

The value  $C \approx 5 \text{ M}$  follows from the internal surface area  $400 \text{ m}^2 \text{ g}^{-1}$  (water adsorption) (7) and, since the  $\text{SiO}_2$  concentration is  $24 \text{ M}$ ,  $\beta = 4.5$ . With  $K_{\text{RH}} = 10^{-7}$  (25) the estimated values of  $b_1$  and  $b_2$  are  $b_1 = 2 \times 10^{-6}$  and  $b_2 = 10^{-7}$ .

Numerical solutions of [4] were obtained by computer calculations using the Crank–Nicholson finite difference scheme<sup>1</sup> with initial and boundary conditions:

$$\gamma(\kappa, \tau = 0) = 0, \quad 0 < \kappa \leq 1,$$

$$\gamma(\kappa = 0, \tau) = 1, \quad \tau \geq 0,$$

$$\partial\gamma/\partial\kappa = 0 \quad \text{at} \quad \kappa = 1.$$

Fig. 5b and c show the two extremes of the computer plots calculated with several  $D_{\text{Na}}/D_{\text{H}}$  values in the range  $10^{-4}$  to 1 with  $K_{\text{RH}} = 10^{-7}$ . The surface areas  $F(\tau)$  below the curves were calculated with spacings of 0.01 in  $F$ . A reliable value of  $D_{\text{Na}}/D_{\text{H}}$  cannot be found from a comparison of the experi-

<sup>1</sup> The programming was performed by Dr. G. J. Visser of the Computing Centre of the Eindhoven University of Technology.

mental with the calculated curves. Deviations from the calculated behavior may be caused by the presence of activity-coefficient gradients, by swelling, and by the lack of a constant pH in our experiments. We interpolated the  $\tau$  values corresponding to the experimental  $F(t)$  values and calculated  $D_{\text{Na}} = \tau x_0^2/t$  and  $D_{\text{H}}$  for different values of the ratio  $D_{\text{Na}}/D_{\text{H}}$ . The mean values of  $D_{\text{Na}}$  and  $D_{\text{H}}$  for two series of experiments are tabulated in Table II. It can be noted that  $D_{\text{H}}$  is nearly independent of  $D_{\text{Na}}/D_{\text{H}}$  in this  $F(\tau)$  range. If  $K_{\text{RH}}$  is taken one order of magnitude higher (lower) (25)  $D_{\text{H}}$  becomes one order of magnitude lower (higher); thus the estimated value of  $D_{\text{H}}$  falls in the range  $10^{-15}$  to  $10^{-13} \text{ m}^2 \text{sec}^{-1}$ . Since the ratio  $D_{\text{Na}}/D_{\text{H}}$  can have a value in the range  $10^{-4}$  to  $10^{-1}$  the value of  $D_{\text{Na}}$  falls in the range  $10^{-19}$  –  $10^{-14} \text{ m}^2 \text{sec}^{-1}$ .

#### ACKNOWLEDGMENTS

The authors are indebted to Mrs. C. Zegers of the Interuniversity Reactor Institute at Delft for the neutron activation analysis of chloride in the silica films and the preparation of double-tracer NaBr, to Mr. J. W. Versteeg for his thickness measurements by the Taly step apparatus and to Dr. G. J. Visser for assistance in the calculations.

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