

# A radiotracer determination of the adsorption of sodium ion in the compact part of the double layer of vitreous silica

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# A Radiotracer Determination of the Adsorption of Sodium Ion in the Compact Part of the Double Layer of Vitreous Silica

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The amount of adsorbed sodium ions in the compact part of the electrical double layer of the vitreous silica electrolyte interface has been estimated at pH 10 with the aid of a sodium-24 and bromide-82 tracer. Etching experiments show a penetration depth of sodium ions in the solid phase less than 0.3 nm; moreover, a gel layer formation at pH 10 is not observed. This experimental evidence is against the application of the gel layer explanation in case of nonporous silica and in favor of the site-binding model.

## INTRODUCTION

In the last decade much experimental and theoretical effort has been made to explain the colloid-chemical behavior of the oxide-water interface. We refer to a recent review article by Wiese *et al.* (1) for the present status in this field. Hunter and Wright (2) have shown that a satisfactory agreement between calculated and experimental diffuse layer potentials can only be obtained when the surface potential  $\psi_0$  is taken less than that given by the Nernst equation for oxides:

$$\psi_0 = 2.303 \frac{RT}{F} (\text{pH}_0 - \text{pH}),$$

where  $\text{pH}_0$  is the pH at which  $\psi_0 = 0$ . Bérubé and De Bruyn (3) pointed out that the Nernst equation is only valid if the surface chemical potential of  $\text{H}^+$  is independent of  $\psi_0$ . Wright and Hunter (4) derived a relation between  $\psi_0$  and pH which is equivalent to Levine and Smith's (5) modified Nernst equation. They showed that this relation may lead to agreement

between measured zeta potentials and theoretical  $\psi_0$  values, but the calculated surface charge densities are much smaller than found experimentally for many oxides. Wright and Hunter, following Lyklema (6), assumed that oxides have a surface gel layer in which counterions can penetrate. Perram *et al.* (7) proposed a mathematical model to describe gel layers. Using reasonable values of adsorption potentials and dissociation constants taken from tables they could account quantitatively for all the data of, e.g., silica by characterizing the interface by a gel layer of thickness 2.0 nm.

A fundamentally different approach is the site-binding model, introduced by Yates, *et al.* (8), in which it is proposed that the adsorbed counterions form interfacial ion pairs with discrete charged surface groups on the impenetrable interface. This model can also account for experimental adsorption isotherms and zeta potentials.

In the case of silica one has to distinguish between precipitated highly porous

silica (9) and pyrogenic nonporous silica (10). The surface charge densities measured on precipitated silica in the presence of 1-1 electrolytes were much greater than those on pyrogenic silica, which is closer in nature to vitreous silica. Perram *et al.* (7) considered their model of a finite disordered gel region to be only of relevance to those systems for which high charges have been reported. Yet, in case of silica they compared their calculated zeta potential values with those measured by Gaudin and Fuerstenau (11) on crushed quartz. Yates *et al.* (8) considered the possibility that their model described an equivalent condenser model involving a porous hydrated oxide surface layer. According to these authors the question of whether or not there is a gel or porous layer at the oxide/electrolyte interface can only be answered by further experimental and theoretical investigation.

Yates and Healy (12) examined precipitated silica by gas adsorption and dissolution rate methods and by measuring the amount of hydrogen-tritium exchange between liquid water and tritium-labeled oxide and compared the results with experimental surface charge vs pH isotherms. They concluded that in the case of precipitated silica a surface gel layer is present, which is permeable to protons and counterions, whereas the interface of silica heated to 800°C is impermeable to both and the surface density of hydroxyl groups is about the same as that for fully hydroxylated quartz crystal surfaces.

In this paper we present the results of radio tracer experiments on vitreous silica rods. The aim is to determine the penetration depth of sodium ions in the solid when this is immersed in a solution containing sodium ions, thus providing experimental evidence whether or not the application of the gel model on nonporous silica is justified. We solved the problem of the discrimination between

sodium ions in the adhering water layer and those desorbed from the interface on rinsing off the rods with acetone, by using a double tracer technique (sodium-24 and bromide-82). After the washing procedure thin layers were etched from the silica rods.

#### EXPERIMENTAL METHODS

*Materials.* Vitreous silica rods (Herasil I, 10-50 ppm aluminum according to the manufacturer's specification) with a diameter of 2 mm.

The radioactive tracers sodium-24 and bromide-82 (half-lives of 15.0 and 35.9 hr, respectively) were obtained from the Interuniversity Reactor Institute at Delft, The Netherlands. For that purpose 11 mg samples of sodium chloride and sodium bromide have been irradiated in the nuclear reactor in a neutron flux of  $1.0 \times 10^{13}$  neutrons/cm<sup>2</sup> sec for 8 hr. At time of measurement of the radioactive tracers (generally 36 to 60 hr after the end of irradiation) the activity amounted to 0.23-0.075 mCi sodium-24/mg sodium and to 0.25-0.16 mCi bromide-82/mg bromide.

The samples were dissolved in 200-400  $\mu$ l water and aliquots were transferred to  $10^{-4}$  M HCl or NaOH solutions to obtain sodium ion concentrations in the order of 0.01 M. The sodium ion concentrations in the latter solutions were checked by neutron activation analyses on 0.5 ml aliquots.

*Zeta potential measurements.* These were performed on rods in 0.01 M NaCl and varying pH with the method described earlier (13). The steps in the pretreatment of the rods were: (i) wiping with lens tissue, (ii) degreasing in condensing vapor of carbon tetrachloride for 20 min, (iii) flaming in a colorless Bunsen burner flame, (iv) immersing in 5% aqueous hydrofluoric acid solution for 2 min, (v) rinsing with water and wiping with lens tissue, (vi) as ii, (vii) as iii

and (viii) equilibrating of the rods in the solution to be measured for at least 20 hr. The degreasing and flaming steps were recommended by Hensley c.s. (14) in adsorption experiments on glass and vitreous silica.

*Radiotracer adsorption experiments.* These were performed on sets of five pieces of rods, which were clamped in a PTFE holder. The pretreatment of the sets of rods was the same as in the zeta potential measurements. Thereafter they were put in polypropylene tubes in which 2.5 ml sodium-24 chloride or sodium-24 bromide-82 containing solutions of pH 4 or 10. The immersion depth was about 45 mm. The tubes were placed in larger ones provided with screw-cap and stored in a jar containing carbosorb to exclude carbon dioxide. After 2 hr standing the washing and etching procedure were applied on one of the sets, the other sets were treated the next day.

The radioactive fractions were counted in a 1 in. well of a 3 × 3 in. NaI (T1) scintillation detector coupled to a 400-channel analyzer (about 9 keV/channel). The counting times ranged from 2000 to 5000 sec, depending on the activity level and were automatically corrected for dead time. The reference solution was prepared by pipetting 30  $\mu$ l of the original radioactive solution into 50 ml of a 1 M NaBr solution and by taking a 3 ml aliquot for counting. The activity measurement in all fractions was based on the 2754 keV gamma peak of sodium-24 and the 1044 keV gamma peak of bromide-82. A straightforward background correction was used in the determination of the area of the 1044 keV peak, lying on the Compton edge of the 1369 keV gamma peak of sodium-24. In the area determination of both peaks all relevant contributions to the uncertainty of the net peak area—due to statistics—were assembled to a final standard deviation.

*Washing and etching procedures.* We

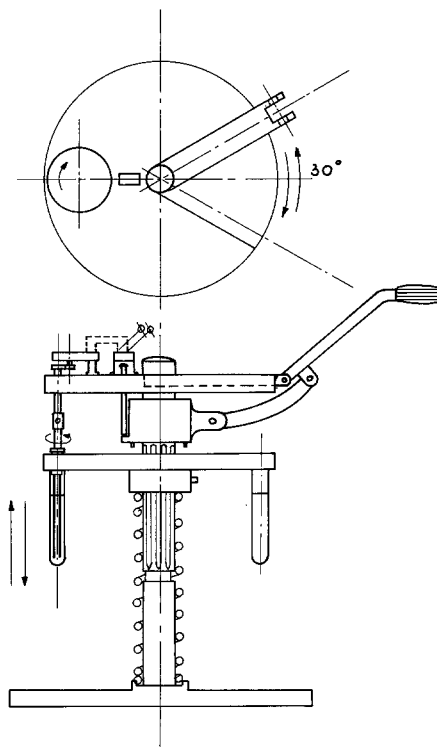


FIG. 1. Tube-changing apparatus.

constructed an apparatus (Fig. 1) to perform the washing and etching procedures in a reproducible way. Twelve tubes, inner diameter 10 mm, are fixed in a circular position on a disk. The set of rods is fastened on the axis of a small electro-motor. By pushing down a handle and turning it over 30° the rods are brought above the next tube and by pushing up the handle the rods are immersed in the solution in the tube and the stirring motor starts to turn slowly (60 rpm). The transfer time from one tube to the next is 1.0 sec.

The washing procedure was established with sodium-24 chloride solutions. Following Long and Willard (15) we started with anhydrous acetone as a rinsing liquid. When two sets of rods, which have been immersed only 2 min in 0.01 M NaCl solutions of pH 4 and 10, respectively, are washed seven times for 5 sec with 3.5 ml acetone and etched twice

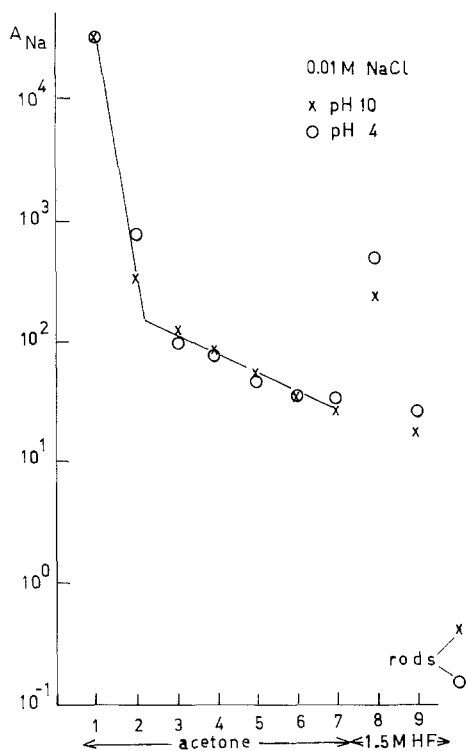


FIG. 2. Variation of count rate (arbitrary units) with washing or etching fraction; washing liquid: anhydrous acetone.

for 5 sec in 2.5 ml 1.5 M HF, the two plots of count rate versus washing fraction are practically the same (Fig. 2). Two linear parts can be distinguished. The first originates from the adhering active solution and we attribute the other to the dissolution of sodium chloride precipitated on the rods by the acetone. Evidence for this assumption is the relatively high count rate of the first etching fraction. Moreover, a few drops of a sodium chloride solution yield a visible precipitate in anhydrous acetone as found in a test-tube experiment. The nearly concentration independent adsorption of sodium ions on vitreous silica and its negative temperature coefficient, reported by Hensley *et al.* (14), may presumably be attributed to the same effect. A small amount of water (4% by weight) in the acetone prevents the precipitation

of sodium chloride. From the first experiments with this rinsing liquid, it was clear that sodium ions are already desorbed during the washings. We continued the experiments with sodium-24 bromide-82 solutions, in order to determine more precisely, the part of the activity in a washing fraction which stems from the desorption process.

The ultimate washing and etching procedures consist of the following steps: seven 1-sec washings with 3.5 ml acetone + water (96:4 m/m), waiting until the adhered acetone has been vaporized (about 5 min), three 1-sec etchings in 2.5 ml 1.5 M HF, after which the rods are placed in distilled water in the last tube.

*Determination of the dissolution rate.* The dissolution rate of Herasil I rods in 1.5 M HF at room temperature was determined. After being subjected to the usual pretreatment procedure, the sets of rods were soaked 24 hr in 0.01 M NaCl at pH 4 (i), at pH 10 (ii) or were stored dry (iii). With the aid of our tube-changing apparatus the sets of rods were etched in 3 ml 1.5 M HF portions for successively 2, 2, 3, 3, 4, and 4 sec. In the cases (i) and (ii) the rods were washed in acetone + water 96:4 m/m before etching and the acetone film was allowed to vaporize because, as was established in preliminary experiments, it decreases the dissolution rate.

The silica in the 3-ml etching fractions was determined by the yellow molybdosilicic acid method for which Lange's (16) directions were modified as follows: The HF solution is poured into a small ethylene bottle and the tube is rinsed successively with 3.0 ml ammonium molybdate solution [80 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 1 liter 0.9 M NaOH] and three times with 3.0 ml 0.5 M  $\text{AlCl}_3$  (in 0.001 M HCl) which are added quantitatively to the HF solution in the polyethylene bottle. The resulting solution is homogenized and after exactly 15 min its ab-

sorbance is measured at  $\lambda = 377$  nm. Standard solutions of 3 ml are prepared from a stock solution containing  $100 \mu\text{g SiO}_2/\text{ml}$   $1.5 M$  HF by suitable dilution with  $1.5 M$  HF. The calibration curve found is linear, notwithstanding the high fluoride concentration in the solutions, between 1 and at least  $30 \mu\text{g SiO}_2/3 \text{ ml}$   $1.5 M$  HF.

The plots of the cumulative amounts of silica found in the successive etching fractions versus the accumulated etching times—including the transfer time from one tube to the next—are linear within the experimental error. They have practically the same slope in the three cases considered. From this slope and the geometrical surface area of the immersed parts of the rods and using a density  $2.2 \text{ g/cm}^3$  of vitreous silica, the dissolution rate  $0.29 \pm 0.02 \text{ nm/sec}$  follows. This value agrees very well with the value taken from Judge's (17) graph, viz,  $0.28 \text{ nm/sec}$  in  $1.5 M$  HF at  $25^\circ\text{C}$ .

## RESULTS

The results of the zeta potential measurements at a constant background of  $0.01 M$  NaCl and various pH values are shown in

Fig. 3. The method used requires the knowledge of the zeta potentials of PTFE in the same solutions and the measured values are also shown in this Fig. 3. Our zeta potential values of vitreous silica are in accordance with Li and De Bruyn's (18) and Prasad and Pooley's (19) zeta potential measurements on crushed quartz in  $0.01 M$  NaCl.

Figure 4 shows a typical result of the experiments in which the rods have been soaked in a  $0.01 M$  NaBr solution at pH 4. After the first two washings the count rate of sodium as well as of bromide decreases exponentially with the number of washings. In the seventh washing fraction no sodium and bromide activity is detectable. The first HF etching fraction of the experiment to which Fig. 4 refers has a low sodium and bromide count rate, which, however, can be attributed to NaBr solution retained in cracks, as follows from the ratio of both count rates. The activity of the rods can be attributed to contamination by NaBr solution (of the order of  $1 \mu\text{g}$ ) at the upper parts of the rods.

Figure 5 gives a typical result of the experiments in which the rods have been soaked in a solution of pH 10. After the first two washings the bromide activity de-

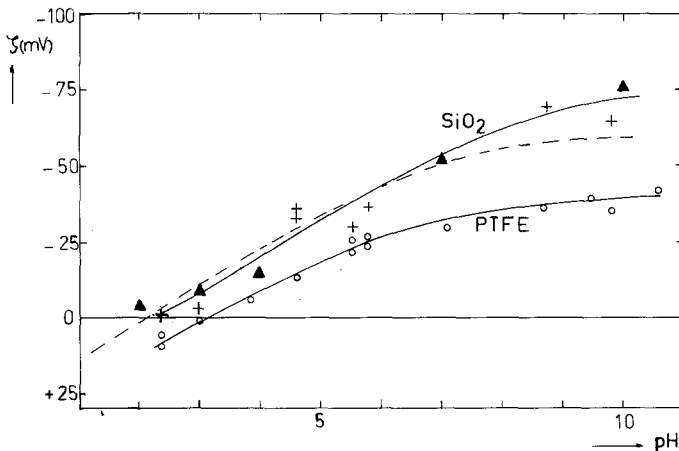


FIG. 3. Variation of zeta potentials of vitreous silica [(+) this study, (▲) Li and De Bruyn, (---) Prasad and Pooley] and PTFE (○) with pH;  $10^{-2} M$  NaCl background electrolyte.

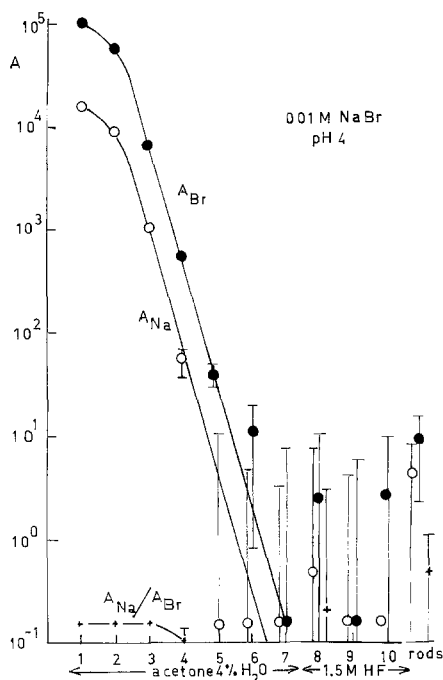


FIG. 4. Variation of count rate (arbitrary units) with washing or etching fraction; rods soaked in 0.01 *M* NaBr at pH 4; (●)  $A_{Br}$ , (○)  $A_{Na}$ , +  $R = A_{Na}/A_{Br}$ .

increases exponentially with the number of washings. This is not the case with the sodium activity. The count rate of even the seventh washing fraction differs statistically significantly from zero. The first etching solution shows a sodium activity, but the count rates of the second and third etching fractions are zero. The sodium and bromide activity of the rods can again be attributed to a slight contamination at the upper parts of the rods.

The exponential decrease of the bromide count rate at pH 4 as well as at pH 10 indicates that adsorption of bromide is absent, as may be expected from the negative zeta potentials in these solutions. The adsorption of sodium at pH 4 is also not detectable, but at pH 10 it clearly occurs. The adsorbed sodium ions, remaining after the seventh acetone washing are removed from the rods by one HF etching of 1 sec. Because bromide adsorption is negligible, the contribution of the desorbed sodium ions ( $A_{Na,des}$ )

to the count rate of the washing fractions can be calculated with the relation:

$$A_{Na,des} = (R - R_{Ref})A_{Br},$$

in which  $R$  is the ratio of sodium and bromide count rates ( $A_{Na}/A_{Br}$ ) in the washing fraction concerned,  $R_{Ref}$  is that of the reference solution. The  $R$  values begin to differ significantly from  $R_{Ref}$  at the third washing fraction. We made an estimation of a lower value of the adsorbed sodium ions by summation of their contributions to the count rate in the third and higher washing fractions and in the etching fractions. This sum is expressed in  $\mu\text{C}/\text{cm}^2$  with the aid of the count rate equivalent to 1  $\mu\text{g}$  sodium found from the count rate of the reference solution, and by assuming a roughness factor 1 in the calculation of the surface area exposed to the NaBr solutions. In Table I the surface densities of sodium ions in the experiments performed at a pH of nominally

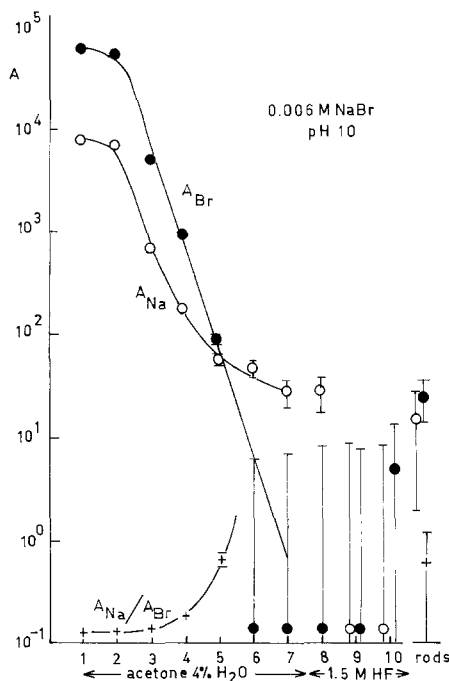


FIG. 5. Variation of count rate (arbitrary units) with washing or etching fraction; rods soaked in 0.006 *M* NaBr at pH 10; (●)  $A_{Br}$ , (○)  $A_{Na}$ , +  $R = A_{Na}/A_{Br}$ .

TABLE I  
Adsorption Data for the Experiments at pH 10

Expt	NaBr concn (M)	Immersion time (hr)	$\sigma_{\text{Na}^+}$ ( $\mu\text{C}/\text{cm}^2$ )	$\sigma_d$ ( $\mu\text{C}/\text{cm}^2$ )	$\sigma_0$ ( $\mu\text{C}/\text{cm}^2$ )	
					This study	Bolt, pH 9.7
G	$5.8 \times 10^{-3}$	3	$7.7 \pm 1.0$	2.2	$-9.9 \pm 1.0$	
H	$5.8 \times 10^{-3}$	21	$6.6 \pm 1.2$	2.2	$-8.8 \pm 1.2$	-9.7
K	$5.8 \times 10^{-3}$	22	$7.0 \pm 1.0$	2.2	$-9.2 \pm 1.0$	
A	$9.7 \times 10^{-3}$	3	$8.5 \pm 1.0$	2.4	$-10.9 \pm 1.0$	-10.7
B	$9.7 \times 10^{-3}$	28	$7.6 \pm 1.6$	2.4	$-10.0 \pm 1.6$	
D	$15.0 \times 10^{-3}$	21	$10.3 \pm 3.5$	2.5	$-12.8 \pm 3.5$	-11.7

10 are summarized. In dummy experiments, however, we found that on standing overnight, these solutions with the rods immersed in them showed pH decreases of about 0.3 unit. We therefore consider these solutions as of pH 9.7. The charge density values in the diffuse layer  $\sigma_d$  in Table I were calculated with the theory of the flat double layer, taking  $\psi_d = \zeta$ . The zeta potential values in solutions other than 0.01 M NaBr were extrapolated from Li and De Bruyn's (18) results. The charge density  $\sigma_0$  due to surface groups follows from the condition of overall electrical neutrality:

$$\sigma_0 + \sigma_{\text{Na}^+} + \sigma_d = 0.$$

#### DISCUSSION

The results of the zeta potential measurements from this paper and from a previous paper (13) show that the vitreous silica used has the same electrokinetic properties as nonporous crushed quartz. As the Nernst equation is also not valid for this material (2) the question rises whether the gel layer theory with a gel layer thickness 2.0 nm (7) must be applied or that the site-binding model (8) is more appropriate.

From our measurements it is apparent that the rapid rise in  $\sigma_{\text{Na}^+}$  and with that also in  $\sigma_0$ , occurs after pH 4, in accordance with literature data on surface charges titratable with acid or alkali (20). The esti-

mated  $\sigma_0$  values at pH 10 agree with Bolt's (20) results (Table I, last column), but are somewhat lower than Abendroth's (10) data. Our desorption (washing) experiments show that the adsorbed sodium ions are not completely present in the diffuse layer as was assumed by Li and De Bruyn (18). Their interpretation of the differences between  $\psi_d$  and  $\zeta$ , based on the electroviscous effect introduced by Lyklema and Overbeek (21) is thus not tenable. The adsorption densities of sodium measured by Li and De Bruyn (18) need only a small correction for the adsorption density of sodium in the diffuse layer, calculable with  $\psi_d = \zeta$ , in order to obtain the adsorption densities of sodium in the compact part of the electrical double layer.

A further advantage of our method is, however, that an indication can be obtained how far sodium ions penetrate into the silica interface. The adsorbed sodium ions are only superficially present, as appears from the desorption of the main part after seven washings of 1 sec in acetone. The remaining ions on the rods are completely removed in one etching of 1 sec in 1.5 M HF in which 0.3 nm silica is dissolved.

We shall now examine whether, the diffusion of sodium ions from a gel layer— with thickness  $L = 2.0$  nm as postulated by Perram *et al.* (7)—during the acetone washings can be responsible for the rapid



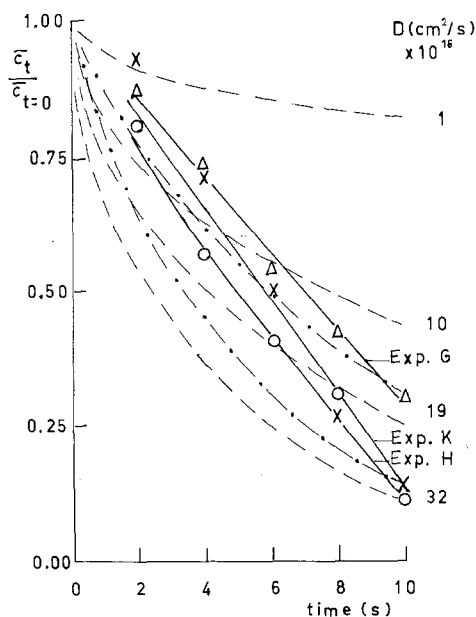


FIG. 6. Variation of the ratio of the mean sodium concentration in a gel layer at time  $t$  and at  $t = 0$  with time. (—) Experimental. Theoretical curves calculated with various diffusion coefficients and initial concentration profiles (---)  $a/C_0 = 1$ ; (-·-)  $a/C_0 \geq 100$ ; thickness of gel layer, 2 nm.

loss of sodium from the silica. We assume that the diffusion starts after the second acetone washing when the sodium concentration in the adhering liquid has attained a low value. Fick's second law is applied to the diffusion out of a slab (22) in which the concentration  $C$  at time  $t = 0$  is assumed to be given by

$$C_{t=0} = C_0 + a \sin \frac{\pi x}{2L},$$

in which  $x$  is the distance to one surface of the slab and  $2L$  is its thickness;  $a$  and  $C_0$  are constants. The other boundary condition is  $c = 0$  for  $x = 0$  and  $x = 2L$  at  $t > 0$ . When  $a$  is given a positive value, there is obtained, in each half of the slab, an initial concentration profile which resembles that resulting from the model proposed by Peram *et al.* (7).

From the solution  $C(x, t)$  of the differential equation we have calculated the mean value  $\bar{C}(t)$  of the concentration in the slab at time  $t$ .

In Fig. 6 the ratio of  $\bar{C}(t)$  and  $\bar{C}(t = 0)$  is plotted versus time for various values of the diffusion coefficient  $D$  and for  $a/C_0 = 0$  and  $a/C_0 \geq 100$ . The experimental values of  $\bar{C}(t)/\bar{C}(t = 0)$ , obtained by dividing the activity remaining on the rods after each washing by the total activity found on the rods, are also shown in Fig. 6. For each washing an effective washing time of 2 sec has been taken into account. From a comparison of the experimental and theoretical curves, it follows that some agreement is only obtained when  $D = (1-3) \times 10^{-15}$  cm<sup>2</sup>/sec together with a high value of  $a/C_0$ . This diffusion coefficient is however much higher than the value found, after reduction to room temperature, from Doremus's (23) and Baucke's (24) data on the interdiffusion of hydrogen and lithium ions in a glass surface at 50°C, even when the greater mobility of sodium ions compared to lithium ions (25) is taken into account ( $1.2 \times 10^{-16}$  cm<sup>2</sup>/sec). This discrepancy between the diffusion coefficients excludes the explanation of the desorption data by a diffusion process from a gel layer with thickness of about 2 nm. Consequently the washing is an exchange process between adsorbed sodium ions on the surface and protons from the water in the acetone-water mixture. Our observation that the dissolution rate in 1.5 M HF is practically the same whether the rods are stored dry or stored in an 0.01 M NaCl solution of pH 10 or 4 provides further evidence against the formation of a gel layer on nonporous silica. This is in accordance with Yates and Healy's (12) findings on heat-treated silica.

Our conclusion is that the gel layer explanation cannot be used in the case of nonporous silica and that for this material the site-binding model as proposed by Yates *et al.* (8) is more appropriate.

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## REFERENCES

1. Wiese, G. R., Yates, D. E., James, R. O., and Healy, T. W., in "M.T.P. Int. Rev. Sci., Physical Chemistry" (J. O. M. Bockris, Ed.), Ser. Two, Vol. 6, p. 53. Butterworths, London, 1976.
2. Hunter, R. J., and Wright, H. J. L., *J. Colloid Interface Sci.* **37**, 564 (1971).
3. Bérubé, Y. G., and de Bruyn, P. L., *J. Colloid Interface Sci.* **27**, 305 (1968).
4. Wright, H. J. L., and Hunter, R. J., *Aust. J. Chem.* **26**, 1191 (1973).
5. Levine, S., and Smith, A. L., *Discuss. Faraday Soc.* **52**, 290 (1971).
6. Lyklema, J., *J. Electroanal. Chem.* **18**, 341 (1968).
7. (a) Perram, J. W., *J. Chem. Soc. Faraday II*, 993 (1973); (b) Perram, J. W., Hunter, R. J., and Wright, H. J. L., *Chem. Phys. Lett.* **23**, 265 (1973); (c) Perram, J. W., Hunter, R. J., and Wright, H. J. L., *Aust. J. Chem.* **27**, 461 (1974).
8. Yates, D. E., Levine, S., and Healy, T. W., *J. Chem. Soc., Faraday I* 1807 (1974).
9. Tadros, T. F., and Lyklema, J., *Electroanal. Chem.* **17**, 267 (1968).
10. Abendroth, R. P., *J. Colloid Interface Sci.* **34**, 591 (1970).
11. Gaudin, A. M., and Fuerstenau, D. W. *Trans. AIME* **202**, 66 (1955).
12. Yates, D. E., and Healy, T. W., *J. Colloid Interface Sci.* **55**, 9 (1976).
13. Smit, W., and Stein, H. N., *J. Colloid Interface Sci.* **60**, 299 (1977).
14. Hensley, J. W., Long, A. O., and Willard, J. E., *Ind. Eng. Chem.* **41**, 1415 (1949).
15. Long, A. O., and Willard, J. E., *Ind. Eng. Chem.* **44**, 916 (1952).
16. Lange, J., *Silikattechnik* **20**, 167 (1969); **21**, 173 (1970).
17. Judge, J. S., *J. Electrochem. Soc.* **118**, 1772 (1971).
18. Li, H. C., and de Bruyn, P. L., *Surface Sci.* **5**, 203 (1966).
19. Prasad, N. A., and Pooley, F. D., *J. Appl. Chem. Biotechnol.* **23**, 675 (1973).
20. Bolt, G. H., *J. Phys. Chem.* **61**, 1166 (1957).
21. Lyklema, J., and Overbeek, J. T. G., *J. Colloid Sci.* **16**, 501 (1961).
22. Jost, W., and Hauffe, K., "Diffusion," Dr. Dietrich Steinkopff Verlag, Darmstadt, 1972.
23. Doremus, R. H., *J. Non-Crystalline Solids* **19**, 137 (1975).
24. Baucke, F. G. K., *Non-Crystalline Solids* **14**, 13 (1974).
25. Doremus, R. H., *Phys. Chem. Glasses* **10**, 28 (1969).