Tritium exchange experiments on thin microporous silica layers

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TRITIUM EXCHANGE EXPERIMENTS ON THIN MICROPOROUS SILICA LAYERS

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The tritium–hydrogen exchange and the tritium distribution in tritium-labelled thin microporous silica layers was studied with a washing and etching technique. The tritium distribution was found to be homogeneous along the whole thickness of the layer. The exchange process can be resolved in three diffusion processes which can be related, in order of decreasing rate, to tritium: (i) in the physisorbed water molecules in the micropores; (ii) in the silanol groups in the micropores; and (iii) in bulk intra-skeletal silanol groups, respectively, in agreement with the description of the microporous silica layer given by Grigorovich et al.

The diffusion rate of the water molecules resembles the diffusion rate of water molecules in ice I. The diffusion coefficient of the hydrogen in the micropore silanol groups ($5 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$) is much higher than the self-diffusion coefficient $D_{\text{H}} \approx 10^{-21} \text{ m}^2 \text{ s}^{-1}$, calculated from the previously studied sodium–hydrogen exchange process in the silica film using the interdiffusion coefficient according to Doremus. However, the former diffusion coefficient is compatible with the diffusion coefficient of the “free” hydrogen ions, calculated from the sodium–hydrogen exchange process using an interdiffusion coefficient according to Helfferich by which the dissociation of the silanol groups in the micropores is taken into account, if the dissociation constant is about 10^{-9} .

1. Introduction

In a previous paper [1] we investigated the sorption of sodium ions by thin microporous silica layers, deposited on vitreous silica rods by the hydrolysis of SiCl_4 . We interpreted this sorption as an interdiffusion of sodium and hydrogen ions. Since we took it for granted that the silanol groups in the hydrous silica layer are dissociated only to a minor extent, we applied an interdiffusion coefficient $\bar{D}$, derived by Helfferich [2], which takes into account the association of H^+ with $\equiv\text{SiO}^-$ groups. Following Helfferich, by “free” H^+ ions we indicate H^+ ions in the silica layer, which do not form part of silanol groups. Since bare protons cannot exist in a condensed phase [3], such “free” H^+ ions must be bound to free electron pairs on oxygen atoms in siloxane bridges, in silanol groups or in water. This binding, however, is much less tight than that of H^+ in silanol groups. The estimated

value of the individual diffusion coefficient $D_{H^+, free}$, varies with the assumed value of the unknown dissociation constant of the silanol groups within the hydrous silica layer. Nevertheless, we can state that our $D_{H^+, free}$ value is many orders of magnitude higher than the D_H value, calculated by Doremus [4,5]. This author assumes that all SiOH groups in the hydrous silica film are dissociated into SiO^- and hydronium ions, and that the latter diffuse freely within the film.

In the terminology of Schwarz et al. [6] an individual diffusion coefficient calculated by Doremus's procedure is an apparent individual diffusion coefficient D_{app} . It can be shown that in the interdiffusion process of sodium and hydrogen ions $D_{H, app}$ is of the order (not equal to) $\alpha D_{H^+, free}$, where α is the degree of dissociation of the silanol groups. Therefore, we and Doremus agree that the diffusivity of hydrogen ions in the film is lower than that of sodium ions; however, we disagree about the reason for the difference. In our view it is the small dissociation of the SiOH groups (not compensated by the higher inherent mobility of dissociated protons); in his view, it is because sodium ions are smaller than hydronium ions.

In the concluding remark of this paper on the interdiffusion of hydrogen and alkali ions in a glass surface, Doremus [4] urged his colleagues to examine other influences on $\bar{D}$. Stimulated by this remark, we [7] investigated the implications of an interdiffusion coefficient that takes into account the association of hydrogen ions and non-bridging oxygen ions, when applied to the experimental concentration profiles in surface layers on silicate glasses, reported in the literature. An essential feature of what we called the extended Boksay–Doremus theory is, that the experimental relative order of the chemical durability of alkali–alkaline earth–silicate glasses can be derived when the glass composition is taken into account in the interdiffusion coefficient.

In this paper we report tritium exchange experiments on thin microporous silica layers, which were performed with the intention of finding experimental evidence for our or Doremus's interpretation of the diffusivity of hydrogen ions in such layers.

2. Experimental

2.1. Silica layers

Five pieces of vitreous silica rods with a circular diameter of 2 mm and length of 8 cm were clamped on a PTFE holder. We call such an assembly a set of rods. Five sets of rods were coated simultaneously with a thin microporous silica layer as fully described previously [1]. An improvement, compared with our previous experiments, consists of the mounting of pieces of heat shrinkable tubing onto the rods, leaving 5 cm of the rods, reckoned from the free ends, bare. After the deposition of the silica layer onto the rods by the hydrolysis of $SiCl_4$, the pieces of tubing

were cut away. One of the sets was sacrificed in order to check the thickness of the layer, which in the present experiments was about $0.3\ \mu\text{m}$ (see below). The amounts of silica on the other sets were determined as part of the tritium exchange experiments.

2.2. Tritium exchange experiments

In these experiments we used a stock solution of tritiated water with an activity of $0.888\ \text{mCi cm}^{-3}$, as determined by comparison with a standard. The silica layers were labelled with tritium by placing the sets of rods in polypropylene tubes containing a sufficient volume of tritiated water (3 ml) to give an immersion depth of more than 5 cm. The rods were kept in the closed tubes for at least two weeks.

Yates and Healy [8] followed the tritium exchange on British Drug House precipitated silica powder after the outgassing of the labelled samples in a vacuum, by which the physically adsorbed water was removed. In order to eliminate possible interference of the diffusion processes by the water molecules penetrating into the pores on placing outgassed samples in water, we performed the exchange experiments mainly on the wet silica films containing molecularly adsorbed labelled water. From many preliminary experiments we concluded that the greater part of the total tritium activity in the microporous silica layers is exchanged by a diffusion process which decays to practically zero in about 100 s.

The following working-method is based on our earlier experiences [9] in discriminating between the radioactivity in the adhering water layer and the radioactivity present in the interface of the rods. Following the labelling, the set of rods was withdrawn from the tritiated water and transported in a closed polypropylene tube to a tube-changing apparatus [9] which was constructed to perform washing and etching procedures in a reproducible way. Twelve tubes, inner diameter 10 mm, can be fixed in a circular position on a disk. The set of rods can be fastened on the axis of a small electromotor. By pushing down a handle and turning it over by 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 s. In order to prevent contamination of the washing or etching liquids in the tubes by tritium adsorbed by the PTFE holder, the length of the axis was such that this holder remained 12 mm above the rim of the tubes. Moreover, a stream of air, saturated with water vapor, was directed perpendicularly on the non-immersed upper parts of the rods.

In the washing/exchange experiments the tubes contained 4.5 ml of distilled water, sufficient for the immersion of the whole microporous silica layer on the rods. After seven 1 s washings, the immersion times were gradually lengthened and the tritium exchange was followed for 10 to 12 days. Thereafter, the set of rods was again immersed in the tritiated stock solution for at least two weeks. In one experiment the tritium exchange was followed on a labelled silica layer dried by outgassing at 0.03 mm Hg for 30 min at 33°C .

In order to obtain an impression of the distribution of the tritium in the silica layers and to determine the thickness of these layers, washing/etching experiments were performed on the wet labelled silica layers on the rods. After four 1 s washings in 4.6 ml of water, the rods were etched in 4.5 ml of 6 mol dm⁻³ HF for four times 1 s, two times 2 s and three times 10 s, successively.

The radioactivity of the washing and etching fractions was determined by conventional liquid scintillation counting using a Packard Tri-Carb Liquid Scintillation Spectrometer, model 3320, and Nuclear Enterprise NE 262 scintillation liquid and NE 262 Standard samples for the determination of the efficiencies of counting as a function of external standard channels ratio. From the washing samples 2 ml aliquots and from the etching samples 0.1 ml aliquots, diluted with 1.9 ml water, were dissolved in the liquid scintillation liquid. Counting periods were 20 or 50 min and the mean of at least five of such countings were taken. Background activities were 90 to 100 counts per minute.

The silica in the etching fractions was determined by the yellow molybdosilicic acid method as described previously [9].

3. Results

3.1. Qualitative description

Figure 1 shows the radioactivity in the first seven washings fractions of the washing/etching experiments and in the four washing fractions of the washing/etching experiments, performed on four sets of rods, as a function of the number of washing operations. After an exponential decrease of the radioactivity along the first three or four washings, the activities deviate from the extrapolated exponential decrease. These deviations must result from the exchange process of tritium within the microporous silica layer and from its outer surface with hydrogen from the washing water. The estimated radioactivity of the completely hydroxylated silica surface is about 40 Bq, calculated with an outer surface area which is 10 times the geometrical macroscopic surface area [1] and with the radioactivity of the tritiated water used.

The exponential decrease of the activity along the first four washings cannot be explained by a complete mixing of the adhering water layer with the washing water, followed by a transfer of a small fraction of the activated washing water through the adhering layer to the next washing water, and so on. In this case, the slope of the straight lines of fig. 1 would be much steeper. Therefore, we suppose that the washing process is, at the beginning, mainly a diffusion of tritium from a stagnant water film ("Nernst-film") to the washing water. With a Nernst-film thickness of about 10 μm we estimate, using eq. (2) of the next sub-section, a diffusion coefficient $D = 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for the water molecules in the Nernst-film.

This D value is about $\frac{1}{50}$ of the self-diffusion coefficient of bulk water at 25°C

Fig. 1. Tritium radioactivity measured in the successive 1 s water washing fractions.

[10] (with the latter diffusion coefficient the tritium from the Nernst-film would be exchanged within 0.1 s).

Since the tritium concentration in the border layer of the Nernst-film, adjacent to the silica/water interface, can differ within 1 s considerably from the value with which the tritium in the silica layer was in equilibrium, the tritium exchange from the silica layer may take place from the beginning of the washing process. However, the tritium from the latter process cannot be discriminated from the tritium, diffused from the Nernst-film, at the beginning of the washings.

We attach an "effective" exchange time of 1 s to the first washing fraction in which the radioactivity deviates significantly from the exponential decrease. Thus, this deviation is plotted in fig. 2 at $t = 1$ s. The difference between the measured and the extrapolated radioactivity of the next washing fraction is added to the previous activity. This total radioactivity is plotted at an effective exchange time found

by adding the immersion time of the washing concerned and the transfer time (1.0 s) to the previous exchange time. Proceeding in this way, we constructed plots of the total tritium radioactivity in solution, resulting from the exchange with the tritium labelled silica layer, as a function of the effective exchange time. These plots are shown in fig. 2. These plots may differ from the real activity versus exchange time plots on account of the unknown exchange during the washings at the beginning.

In the next sub-section we shall see that the radioactivity versus washing time data cannot be fitted by a single diffusion process. Three processes can be distinguished: a fast, a less fast and a slow process. We are mostly interested in the second process, because this process can be linked to the diffusion of tritium from the labelled silanol groups in the micropores. Since the resolution of the exchange process in these three processes is performed starting from the long time side, a possible distortion of the activity versus exchange time plots at the short time side has practically no influence on the calculated value of the diffusion coefficient of the second process.

In fig. 3 a typical result of the etching experiments is shown. In this figure the cumulative amounts of silica etched off and the cumulative amounts of the radioactivities in the etching fractions are plotted as a function of the accumulated etching times (including the 1 s transfer times). The steep part of the silica curve results from the dissolution of the hydrous silica layer and the slightly sloping part

Fig. 2. Cumulative amounts of tritium radioactivities in the washing fractions as a function of the accumulated effective washing times.

Fig. 3. Cumulative amounts of silica etched off and cumulative amounts of tritium radioactivities in the etching fractions as a function of the accumulated etching times [exp. 2 (HF)].

from the dissolution of the vitreous silica core. We take the point of intersection of the extrapolated linear parts as a measure for the thickness of the hydrous silica layer. From our previous experiments [1] we know that $1 \mu\text{g}$ of SiO_2 per cm^2 is equivalent to about 7 nm of thickness. As the geometrical macroscopical surface area of the silica layer is 15.7 cm^2 , $1 \mu\text{g}$ of SiO_2 in the present experiments is equivalent to about 0.45 nm.

The radioactivity curve shows likewise a steep and a flat part and the extrapolated linear parts have an intersection point at an etching time somewhat lower than that of the intersection point of the silica curve. This can be expected because the exchange process proceeds during the etching. From the radioactivity curve, in comparison with the silica dissolution curve, we conclude that the tritium is homogeneously distributed through the hydrous silica layer. The radioactivity in the layer is estimated from the intersection point in fig. 3 to which is added the amount of radioactivity perceptibly exchanged during the washings, diminished by the amount of activity still present at the beginning of the HF treatment in the adhering water layer, as can be estimated from the extrapolated straight lines of fig. 1. This activity value can be lower than the real total activity in the layer on account of the imperceptible exchange during the first three washings, just like the activities of fig. 2. The thickness and activity data of the four sets of rods are tabulated in table 1.

Table 1
Data of the tritium exchange and etching experiments on tritium-labelled thin microporous silica layers (based on the exchange curves of fig. 3)

Experiment	Thickness		Total radio activity (Bq)	Diffusion coefficients			Initial amount of tritium in the film			$\sum_i A_i^0$ (Bq)
	SiO ₂ (μg)	L ^a (nm)		D ₂	$\frac{D_2}{\text{nm}^2 \text{ s}^{-1}}$	D ₃	A ₁ ^{0 b} (Bq)	A ₂ ^{0 c} (Bq)	A ₃ ^{0 c} (Bq)	
0 (HF)	635	285								
1 (H ₂ O)		290	1092	1250	49	0.24	722	319	36	1077
1 (HF)	650	290	875							
2 (H ₂ O) d)		290	(365)	(800)	(14)	(0.07)	(280)	(66)	(28)	(374)
2 (HF)	650	290	1130							
3 (H ₂ O)		330	854	1100	56	0.24	465	349	22	836
		(295) e)		(890)	(45)	(0.19)	(465)	(349)	(22)	(836)
3 (HF)	735	330	790							
4 (H ₂ O)		280	1391	800	56	0.17	1056	341	21	1418
4 (HF)	625	280	880							

a) 1 μg SiO₂ $\approx$ 0.45 nm.

b) 3.29 $\times$ 10⁷ Bq corresponds with 1 g H₂O.

c) 2.96 $\times$ 10⁸ Bq corresponds with 1 g or 1 mol OH group.

d) After outgassing at 0.03 mm Hg for 30 min at 33°C.

e) Mean value of five sets of rods; inserted to show how uncertainty in thickness works on the resolution of the exchange curve.

3.2. Quantitative treatment of the exchange curves

The exchange rate may be controlled either by diffusion within the hydrous silica layer or in the Nernst-“film”. The half-time for Nernst-film diffusion control would be about 40 ms, estimated (see ref. [2]) with a Nernst-film thickness of 10 μm , a silica layer thickness of 0.3 μm and with a diffusion coefficient $D \approx 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ of the water molecules in the Nernst-film, as estimated in the previous sub-section. This excludes Nernst-film diffusion control and we shall treat the exchange rate as “particle” diffusion controlled.

In isotopic exchange experiments the system exchanger-solution is in chemical equilibrium except for isotopic distribution. When the masses of the isotopes are nearly equal there are no gradients of electrical potential in the solution or exchanger and no gradient of activity coefficients. Then, the flow of isotope i , J_i , at any point in the exchanger is given by Fick's first law

$$J_i = -D_i \text{grad } C_i, \quad (1)$$

where D_i is the self-diffusion coefficient and C_i is the concentration.

Scholze et al. [11,12] found a distinct isotopic effect for the dealcalization of glass surfaces by treatment with 0.1 N HCl in H_2O or with 0.1 N DCL in D_2O . However, although the mass ratio can be up to three in the tritium-hydrogen exchange process, we can apply eq. (1) as a first approximation to our tracer experiments ($\approx 0.3 \text{ ppm T}$), since then the interdiffusion coefficient is practically equal to the self-diffusion coefficient of the minor component.

Since the thickness of the silica layers is negligible compared with the radius of the rods, we can treat the diffusion out of the silica layer as a diffusion out of a slab of which one surface is impermeable. The mean value of the concentration $\bar{C}_i(t)$ of the diffusing isotope, left in such a slab after an immersion time of t (s) in a bath in which the isotope concentration in the bulk solution remains essentially zero is given by [13]:

$$\bar{C}_i(t) = \frac{8C_i^0}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp \left[- \left(\frac{(2j+1)\pi}{2L} \right)^2 D_i t \right], \quad (2)$$

when at time $t = 0$ the concentration C_i^0 is constant along the whole thickness L of the slab.

The radioactivity curves of fig. 2 represent the amount of tritium diffused out of the layer at time t . The radioactivities $A_i(t)$ are proportional to

$$SL [C_i^0 - \bar{C}_i(t)],$$

where S is the macroscopical geometrical surface area of the layer. Application of eq. (2) shows that the experimental exchange curves cannot be fitted by one diffusion process, even when the possible deviations of these curves from the real ones are taken into account. In a plot with a logarithmic time scale, the theoretical curves

have a short tail, thus, the steep part at the left hand side of the curves of fig. 2 can only be fitted by a process which decays to practically zero after about 100 s. In fact, on closer examination three processes must be distinguished, a fast, a less fast and a very slow process. The last process was still in progress when the experiments were broken off.

In order to apply eq. (2) we must convert the radioactivity data to radioactivities present in the layer. For the analysis we assume that at the end of the last washing all tritium has been exchanged. Since the tritium involved in the very slow process is only a small fraction of the total tritium in the layer, this assumption has no serious consequences for the other two processes for which equilibrium has practically been attained at the end of an experiment. Then, the amount of tritium in the last washing is equal to the amount of tritium in the layer at the end of the second last washing. The tritium radioactivities in both last washings are added to find the radioactivity at the end of the third last washing, and so on. In fig. 4 the right-hand curve (with right-hand vertical scale) has been constructed in this way from the data of experiment 4 (H_2O). This curve shows mainly the decay of the third process. By trial and error a theoretical fit of eq. (2) to this curve is obtained, yielding D_3 and A_3^0 expressed in Bq. The theoretical values at time t are subtracted from the total radioactivity versus time curve. This results in the middle curve of fig. 4, which has

Fig. 4. Resolution of the radioactivity, left in the hydrous silica layer, versus washing time curve in three diffusion processes [exp. 4 (H_2O), table 1]. The open circles represent experimental values (3) or after subtraction of calculated curves [(1) and (2)] and the crosses the calculated values.

been plotted with another vertical scale. A theoretical fit of eq. (2) yields D_2 and A_2^0 . After subtraction of the theoretical values of the second process from the second radioactivity curve, we obtain the curve at the left hand side of fig. 4, representing the decay of the fast process. We note that the fitting of eq. (2) to the middle curve cannot be made perfect in this case on account of the tail of this curve, which may be caused by the use of a too low A_3^0 value. However, compared with the A_2^0 value the deviations are only small.

Since we found that the tritium radioactivity is homogeneously distributed along the whole thickness of the hydrous silica layer, the fast decaying diffusion process cannot be related to a gel layer of hydrolysed material at the surface of the silica layer. Therefore, we also used the thickness L of the silica layer in the procedure of fitting eq. (2) to the left-hand side curve of fig. 4, which yields D_1 and A_1^0 , which is proportional to SLC_1^0 .

This procedure of splitting up the exchange curve was applied to the other experiments and in fig. 5 the results of experiment 3 (H_2O) are also shown. The D_i and A_i^0 values found are shown in table 1. The A_1^0 and D_1 values in table 1 must be considered to be the lowest estimates on account of the effective times used. The highest estimates of A_1^0 and D_1 are found when the washing times are counted from the first moment of contact of the tritiated rods with the washing water. This

Fig. 5. Resolution of the radioactivity, left in the hydrous silica layer, versus washing time curve in three diffusion processes [exp. 3 (H_2O), table 1]. The open circles represent experimental values (3) or after subtraction of calculated curves [(1) and (2)] and the crosses the calculated values.

increases the times in figs. 4 and 5 by 6 and 8 s respectively. The values of A_2^0 , D_2 , A_3^0 and D_3 are insignificantly influenced by this, but the A_1^0 and D_1 values of the theoretical fits to the shifted curves are increased by about 50%.

4. Discussion

Grigorovich et al. [14] studied silica layers, deposited on the surface of silicon prisms by the hydrolysis of SiCl_4 , using the method of multi-attenuated total internal reflection infrared spectroscopy. The layers have a homogeneous, microporous structure with pore sizes close to the size of water molecules. Silanol groups in these micropores undergo fast deuterioexchange, whereas the deuterioexchange with bulk intra-skeletal silanol groups only taken place after several days of contact with D_2O vapor. The silanol groups in the micropores are the adsorption sites for physisorbed water, which is completely removed by evacuation at 10^{-2} – 10^{-3} mm Hg for 30 min at 35°C . The internal specific surface of the films determined from the adsorption of water vapor was about 380 – $400\text{ m}^2\text{ g}^{-1}$ [14,15].

The tritium diffused out of the hydrous silica layer in our experiments can be linked, in order of decreasing rate, to the labelled physisorbed water molecules, to the labelled silanol groups in the micropores and to the labelled bulk intra-skeletal silanol groups, respectively.

The mobility of the physisorbed water molecules is so high, that during the transporting and mounting steps, a significant fraction of the tritium can be lost by evaporation of physisorbed water. Moreover, unknown amounts of tritium are exchanged during the first three or four washings. This can explain the differences in the total measurable tritium radioactivities found in the exchange and etching experiments (column 4 of table 1).

From the tritium radioactivities coming from the physisorbed water (A_1^0) we can estimate the internal surface area, using a surface area of 0.25 mm^2 per water molecule [15]. The results, based on the lowest and highest estimates of A_1^0 , are shown in column 2 of table 2. The order of magnitude of the estimated surface area agrees with the value ($400\text{ m}^2\text{ g}^{-1}$) reported by Grigorovich et al. [14] and by Slotin et al. [15].

The diffusion coefficient D_1 is remarkable because its value is only one order of magnitude lower than the equal self-diffusion coefficients of ^2H , ^3H and ^{18}O tracers in ice I [16–18] extrapolated to room temperature. Since the findings on ice I suggest that intact water molecules are able to migrate through the ice lattice [19], we propose, on the basis of the order of magnitude of D_1 , that intact water molecules are likewise able to migrate in the micropores of the hydrous silica layer.

We note that Scholze et al. [11] also reported a rapid $\text{D}_2\text{O}/\text{H}_2\text{O}$ exchange in the gel layer of a dealkalised glass. The estimated order of magnitude of the diffusion coefficient of this exchange process is equal to our D_1 value ($10^{-15}\text{ m}^2\text{ s}^{-1}$).

Notwithstanding the different amounts of molecularly adsorbed water in the

Table 2
Surface area and silanol groups, calculated from A_1^0

Experiment	S.A. ^{a)} (m ² g ⁻¹)	C _{OH(2)} (mol dm ⁻³)	C _{OH(3)} (mol dm ⁻³)	R ^{b)}
1 (H ₂ O)	269–444	2.37	0.26	1.13–1.87
3 (H ₂ O)	154–241	2.28	0.16	0.67–1.05
4 (H ₂ O)	402–614	2.62	0.15	1.55–2.37

^{a)} Calculated with surface area per water molecule: 0.25 nm²; and mass film = mass SiO₂ + mass H₂O.

^{b)} Ratio of water molecules in the micropores to micropore silanol groups.

three exchange experiments on wet silica layers, the amounts of tritium radioactivities A_2^0 , corresponding to the silanol groups in the micropores, are nearly constant (column 9 table 1). The amounts A_3^0 of bulk intra-skeletal silanol groups are much lower.

The radioactivity $A_2^0 = 66$ Bq, found in the exchange experiment on vacuum dried labelled silica layers [exp. 2 (H₂O)], is much lower than the A_2^0 values (≈ 340 Bq), found in the experiments on wet labelled silica layers. It is remarkable that the total radioactivity ($\Sigma A_i^0 = 374$ Bq) in the dried silica layers is nearly equal to $A_2^0 + A_3^0$ of the wet experiments. Presumably, the tracer originally present only in silanol groups in the vacuum dried labelled silica layer, is partially transferred to the non-labelled water molecules, entering the empty micropores when the dried silica layer is brought into contact with non-labelled water. As can be seen from the low D_2 value of exp. 2, the penetrating water molecules also disturb the diffusion processes, as was expected (see section 2.2).

In table 2, the concentrations of both types of silanol groups are shown, which have been calculated from the radioactivities A_2^0 and A_3^0 of table 1. In the last column of table 2 the ratio of molecularly adsorbed water molecules to silanol groups in the micropores is also shown, calculated with the lowest and highest estimates of A_1^0 .

The fact that the tritium diffusion out of the silica layer cannot be described as a single diffusion process but must be resolved into two categories: tritium coming from physisorbed water and tritium coming from silanol groups, refutes Doremus's assumption that the hydrogen ions in the silica layer exist to a significant fraction as hydronium (H₃O⁺) ions which are not tightly bound to the negative silicate groups. This refutation can also be based on quantitative data if it is assumed that the mobility of a species in a tracer diffusion experiment is equal to the mobility of that species, obtained from an interdiffusion experiment, involving concentration and electrical potential gradients. Then we can compare the diffusion coefficients, calculated from our previous results [1], with the diffusion coefficient D_2 of the present paper. If Doremus' interdiffusion coefficient is applied to our previous

results, we find $D_H \approx 10^{-21} \text{ m}^2 \text{ s}^{-1}$ [20] and this value is many orders of magnitude smaller than the D_2 value ($\approx 5 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$) found in the present paper.

We shall now verify whether the present result is compatible with $D_{H^+, \text{ free}}$ found by application of Helfferich's [2] interdiffusion coefficient to our previous results. Consider the equilibrium

where B represents a free electron pair on oxygen atoms in siloxane bridges, silanol groups or in water molecules. In abbreviated form:

The self-diffusion coefficient D_2 of the present paper is an apparent self-diffusion coefficient $D_{H, \text{ app.}}$, because the exchange process was treated as if there were no binding between H^+ and $\equiv\text{SiO}^-$. Schwarz et al. [6] proved that for tracer diffusion experiments the relation

$$D_{H, \text{ app.}} = \alpha D_{H^+, \text{ free}}, \quad (4)$$

where

$$\alpha = C_{H^+}/(C_{\text{OH}} + C_{H^+}) \approx C_{H^+}/C_{\text{OH}},$$

holds, when the equilibrium (3) is instantaneous compared with the exchange process. In a pure silica $C_{\text{O}^-} = C_{H^+}$, and thus

$$\alpha = (K_{\text{OH}}/C_{\text{OH}})^{1/2}, \quad (5)$$

where $K_{\text{OH}} = k_f/k_r$ is the dissociation constant of eq. (3).

In our previous paper [1] we used $C_{\text{OH}} \approx 5 \text{ mol dm}^{-3}$, estimated from the surface area $400 \text{ m}^2 \text{ g}^{-1}$ [14,15] by assuming one H_2O molecules adsorbed per one silanol group. From the present results we know $C_{\text{OH}} \approx 2.4 \text{ mol dm}^{-3}$ (table 2). Therefore, we recalculated $D_{H^+, \text{ free}}$ as a function of K_{OH} and plotted these values in fig. 6. In fig. 6 we have also plotted $D_{H^+, \text{ free}}$, calculated with eqs. (4) and (5), as a function of K_{OH} , using

$$D_{H, \text{ app.}} = D_2 = 5 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}.$$

The point of intersection

$$D_{H^+, \text{ free}} = 2.6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}, \quad K_{\text{OH}} \approx 10^{-9}$$

gives the value which K_{OH} must have if our interpretation is correct. This value, $K_{\text{OH}} \approx 10^{-9}$ differs by only one order of magnitude from the range $10^{-6} - 10^{-8}$, estimated by Dugger et al. [21] for surface silanol groups of amorphous silica, but is somewhat higher than $K_1 = 10^{-9.46}$ of orthosilicic acid. (We note that if D_2 is corrected with a factor $3^{1/2}$ to obtain the value of ^1H instead of ^3H we obtain

Fig. 6. $D_{H^+, free}$ as a function of K_{OH} . (a) From previous [1] results of sodium–hydrogen exchange recalculated with $C_{OH} = 2.4 \text{ mol dm}^{-3}$. (b) Present investigation, from D_2 using eqs. (4) and (5).

$K_{OH} = 10^{-9.4}$.) Because $K_{OH} \approx 10^{-9}$ is an acceptable value if compared with these K values, we conclude that the present and previous results are compatible.

With $K_{OH} \approx 10^{-9}$ the estimated value of $D_{H^+, free}$ from the sodium concentration profiles of Dole glass [7] becomes

$$D_{H^+, free} = 7.4 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}.$$

Since this value is of the same order of magnitude as the value found in the present paper ($2.6 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$), this result can be put forward as additional support for our interpretation of the hydrogen diffusivity.

From eq. (5) with $K_{OH} = 10^{-9}$ we find $\alpha \approx 2 \times 10^{-5}$, thus only a small fraction of the silanol groups is dissociated. However, the magnitude of α is not a sufficient criterion to explain the experimental fact that the tritium leaves the silica layer in different diffusion processes. If e.g. it is assumed that k_r is equal to the rate constant for reactions of hydrogen ions with bases in aqueous solution (order of magnitude 10^{10} to $10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [22]), then the value of k_f would be 10 to 100 s^{-1} . It seems to us that such a k_f value cannot be compatible with the above-mentioned fact. Of course k_r can be orders of magnitude lower than the value assumed above. Another possibility is that K_{OH} is some orders of magnitude lower. It should be noted that, on account of assumptions made in the elaboration of and on

account of experimental errors in the results of especially the sodium–hydrogen exchange experiments, the point of intersection of the two lines in fig. 6 is still liable to shift. Thus, a lower K_{OH} value combined with a higher $D_{H^+, free}$ value, is quite possible. However, such combinations of lower K_{OH} and higher $D_{H^+, free}$ values do not invalidate the support from the calculations on Dole glass from our point of view. Anyhow, the resolution of the total exchange into different processes was only possible on account of the very different rates of the single processes.

5. Conclusion

The tritium diffused out of a micro-porous silica layer cannot be described by a single diffusion process, but must be resolved into two categories. This refutes Doremus's [5] assumption that the hydrogen ions in the hydrous silica layer exist to a significant fraction as hydronium ions. The two categories can be identified as: tritium coming from physisorbed water and tritium coming from silanol groups.

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