

INFRARED SPECTROSCOPIC STUDY OF THE HYDRATION OF POROUS GLASS

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Dedicated to Academician O. Wichterle at the occasion of his 75th birthday.

Infrared spectra of mesoporous and macroporous siliceous glasses were measured in the native state and after silylation, at various contents of H₂O and D₂O. By analysis of these spectra it was found that water is bound to the glass surface by strong hydrogen bonds between the water molecules and isolated Si—OH groups; capillary condensation was observed only in native mesoporous glasses.

The aim of this work was to clarify the connection between the surface structure of amorphous silicon oxide and its ability to bind adsorbed water, as well as to follow the degree of water association in the adsorbed state. Samples of porous glass, i.e. amorphous SiO₂ with well defined porous structure, were studied. The present study of this material is an extension of our spectroscopic studies of the hydration of highly disperse silicate materials of natural origin^{1,2}.

Porous glass is amorphous SiO₂ of large specific surface, with a narrow distribution of pore size. Following the suggestion of Dubinin accepted by IUPAC, we classify porous glass as microporous, with pore diameter $d < 5$ nm, mesoporous ($5 < d < 50$ nm) and macroporous with $d > 50$ nm (ref.³). Concerning the water affinity of porous glass, the content and ordering of silanol (Si—OH) groups is important. The latter are classified as internal and surface groups⁴. The internal Si—OH groups are situated in the bulk of the glass and do not participate in the surface processes. The surface silanol groups are further classified as isolated (free) and vicinal (mutually hydrogen-bonded). According to Kiselev and Lygin⁵, the surface Si—OH groups can undergo mutual hydrogen bond interaction only when their O—H...O distance is smaller than 0.30 nm.

In IR spectra of porous glasses, three weak absorption bands can be identified in the wavenumber range 4 000—1 400 cm⁻¹, at 2 000, 1 880 and 1 640 cm⁻¹, corresponding to SiO₂ absorption⁶. Dehydrated porous glasses exhibit further three absorption bands of Si—OH groups; their intensities and wavenumbers depend on

the temperature of dehydration. The H-bonded surface Si—OH groups absorb in the range $3\,500\text{--}3\,550\text{ cm}^{-1}$. These silanol groups are the least thermostable, being partially dehydroxylated already at temperatures above 200°C . Free Si—OH groups absorb at $3\,740\text{ cm}^{-1}$ and are thermally stable up to about $1\,000^\circ\text{C}$ (ref.⁷). Chukin and Malevich⁸ describe enhanced absorbance of the band at $3\,740\text{ cm}^{-1}$ after heating of porous glass above 300°C . Internal Si—OH groups absorb at $3\,600\text{--}3\,650\text{ cm}^{-1}$ and their dehydroxylation occurs in the range $300\text{--}600^\circ\text{C}$ (refs^{7,8}). In infrared spectra of hydrated porous glasses, absorption bands of water stretching vibrations can be identified around $3\,400\text{ cm}^{-1}$, and of bending vibrations at $1\,620\text{--}1\,640\text{ cm}^{-1}$. Hydration of porous glasses is accompanied by the disappearance of the absorption band of free Si—OH at $3\,740\text{ cm}^{-1}$ in consequence of hydrogen bond (Si—OH \cdots OH₂) formation^{6,7}.

Spectral studies of hydrogen bonds between surface silanol groups and water are complicated by the simultaneous existence of hydrogen bonds between water molecules. In the range of OH stretching vibrations, these two types of hydrogen bonds practically cannot be differentiated. Therefore in order to supplement our understanding of the mode of interaction between surface Si—OH groups and water, besides water adsorption, also the adsorption of dioxane was studied in this work. Dioxane was selected because its molecules do not contain OH groups and therefore do not form mutual hydrogen bonds, but can undergo hydrogen bond interactions with OH groups of other compounds. To elucidate the hydration mechanism of amorphous silicon oxide, porous glass hydrophobized by trimethylchlorosilane was also used. By means of this agent, the surface Si—OH groups could be partly eliminated.

EXPERIMENTAL

A series of porous glass samples for GPC, by Electro-Nucleonics, Inc., was selected, with pore diameters 8.5 to 32.4 nm (mesoporous glass) and 53 to 286.9 nm (macroporous glass³).

The porous glass samples were dehydrated by evacuation for 40 h at 220 and 350°C in a quartz tube, or by drying at 30°C and 5% rel. humidity. The samples dehydrated at elevated temperature were further subjected to irreversible hydrophobization (silylation) by trimethylchlorosilane: they were exposed to vapours of this agent at $20\text{--}25^\circ\text{C}$ for 48 h , and subsequently heated to 220°C for 2 h (refs^{9,10}). Both dehydration and silylation were performed in a sealed quartz tube over P_2O_5 . In addition, the sample of mesoporous glass (11.6 nm), dehydrated at 220°C , was reversibly hydrophobized by Nujol for comparison (by means of a solution of Nujol in CCl_4 which was evaporated at 80°C).

The series of porous glass samples, i.e. both the original non-silylated as well as the silylated samples were hydrated for 30 days over a saturated K_2SO_4 solution at $20\text{--}25^\circ\text{C}$, corresponding to 97% rel. humidity¹¹. Selected samples of non-silylated mesoporous glasses were further hydrated over saturated $\text{Ca}(\text{NO}_3)_2$ solution at 56% rel. humidity¹². With mesoporous glass of pore diameter 11.6 nm , dehydrated at 220 and 350°C , adsorption of 1,4-dioxane from the vapour phase was followed spectroscopically. With this sample (after dehydration at 220°C) the course

of deuteration by D_2O , (99.5% purity) in the vapour phase was also followed before silylation and after it.

The IR spectra of the studied porous glass samples were measured with a Perkin-Elmer 580B spectrometer, connected on-line with the Tracor-Northern 4 000 computer. The spectra were measured in the range $4\ 000-1\ 400\text{ cm}^{-1}$, and normalized with respect to the absorbance of the SiO_2 band at $1\ 880\text{ cm}^{-1}$ which was selected as the analytical internal standard. In most cases, the porous glass samples were measured freely spread out in a thin layer in a demountable cell with CaF_2 windows. For measurements of the course of D_2O , H_2O and dioxane adsorption, the samples were pressed into a Teflon film and measured in a gas cell with $NaCl$ windows. Dehydrated porous glasses are highly hygroscopic. Therefore all manipulations with these samples were carried out in a transportable dry box with rubber gloves. The box was flushed with air dried in the Perkin-Elmer drying tower and passing a layer of silicagel.

The contents of water adsorbed in porous glasses, m , was determined as the mass of water referred to unit mass of dry porous glass. In the original non-silylated samples hydrated at 97% rel. humidity, m was determined gravimetrically from TG and DTG curves obtained by means of the instrument Derivatograph. In silylated porous glasses and in non-silylated samples hydrated at 56% rel. humidity, the water contents was determined from the relation

$$m = \frac{\epsilon(SiO_2) \int A \, d\nu}{aI} \quad (1)$$

using the approximation

$$\int A \, d\nu = A \Delta\nu_{1/2}, \quad (2)$$

where A and $\Delta\nu_{1/2}$ are the maximum absorbance and half-width of the band of H_2O bending vibrations (ν_2), $\epsilon(SiO_2)$ is the absorbance coefficient of the SiO_2 band at $1\ 880\text{ cm}^{-1}$ determined with a Nujol suspension containing a known amount of porous glass, and a is the fixed absorbance value of this band, with respect to which the IR spectra were normalized. The integrated intensity coefficient I of the ν_2 band of adsorbed water was calculated from relation (1) with known absorbance and half-width values of ν_2 bands, and the mass contents of adsorbed water m measured gravimetrically in non-silylated porous glass samples.

The specific surface values shown in Table II were measured by the method of dynamic nitrogen desorption with the instrument Quantasorb (Quantachrom Corp., U.S.A.) and evaluated in the range of the linear portion of the BET isotherm at a single concentration value.

RESULTS

A comparison of IR spectra of porous glasses dehydrated at various temperatures revealed that the wavenumbers of Si—OH stretching vibrations slightly depend on the dehydration temperature (Table I). The absorption band intensities in the range of OH stretching vibrations change but little in the dehydration temperature range 30 to 220°C . After dehydration at 350°C , the absorption band of bound Si—OH groups disappears almost completely, with a simultaneous intensity increase of the absorption of free Si—OH groups⁸. With all absorption bands of silanol groups, a small increase in the wavenumber of the band maximum was observed with increasing dehydration temperature (Table I).

With increasing pore size, i.e. with decreasing specific surface, the absorbance of surface Si—OH groups bands decreases for dehydrated porous glasses. With hydrated samples, the absorbance of H₂O bands decreases, and this is in most cases accompanied by a decrease in the wavenumber of the absorption band of water bending vibrations (Table II). The largest differences in the intensities and wavenumbers of ν_2 absorption bands are observed at vapour tensions near to saturation (97% rel. humidity) for mesoporous and macroporous glasses. Mesoporous glasses hydrated under these conditions exhibit very strong broad absorption bands at 3 400 and 1 628–1 638 cm⁻¹ (Fig. 1). Macroporous glasses, on the other hand, at vapour tensions near to saturation exhibit relatively weak absorption bands of water at 3 400 and 1 612–1 621 cm⁻¹ (Fig. 2).

At a given pore size, the absorption bands of adsorbed water decrease with decreasing relative humidity of air. This is particularly marked for mesoporous glasses, where a decrease in relative water vapour tension by about one half leads to a decrease in the integrated intensity of ν_2 bands of adsorbed water roughly by an order of magnitude. On the other hand, the wavenumber of the ν_2 band shows little dependence on the relative air humidity at which the porous glasses have been hydrated (Table II). Also during stepwise dehydration and rehydration of porous glasses, the wavenumber of the deformation band of adsorbed water exhibits little dependence on water contents (Figs 1a, b). (At low humidity values, the wavenumbers of H₂O stretching vibrations are not mutually comparable, as under these conditions their absorption bands are deformed by the absorption of surface bound Si—OH groups around 3 500 cm⁻¹.)

Adsorption of 1,4-dioxane vapours on porous glass is accompanied by pronounced spectral changes in the range of OH stretching vibrations. Already after very short

TABLE I

Wavenumber values of Si—OH absorption bands in porous glasses dehydrated at various temperatures (cm⁻¹)

T, °C	ν_{OH} for Si—OH groups			Curve D in Fig.
	surface		internal	
	free	bound		
30	3 735	3 500—3 520	3 620	1b
220	3 736	3 550—3 570	3 640	3b
350	3 743		3 650—3 670	1a, 3a

TABLE II

Characteristics of porous glass samples hydrated at relative air humidity 56% (A) and 97% (B). Symbols: d pore diameter, V specific volume of pores, S specific surface of pores, ν_2 wavenumber of the band of adsorbed water, m content of water, φ pore filling, m' water content after silylation

d nm	$\Delta d/d$ %	V $\text{cm}^3 \text{g}^{-1}$	S $\text{m}^2 \text{g}^{-1}$	A		B			
				ν_2 cm^{-1}	m mass %	ν_2 cm^{-1}	m mass %	φ vol. %	m' mass %
8.5	19	0.65	216.6			1 628	85	100	2.8
11.6	8.6	0.78	155	1 632	5.5	1 638	78	100	1.9
16.9	9.6	1.00	161			1 635	104	100	1.7
25.9	8.2	1.31	118	1 631	4.5	1 636	39	29	—
32.4	4.2	1.39	79			1 636.5	18.6	10.1	2.8
53.0	6.7	0.87	43	1 618	1.0	1 621	1.4	1.5	2.6
72.9	6.4	0.77	24.9			1 614.5	1.0	1.3	1.2
101.7	7.4	1.22	27.9	1 613	1.0	1 612	2.0	1.7	1.7
148.9	6.4	1.16	17.6			1 613	1.3	1.3	1.8
208.4	6.1	0.87	8.2	1 613	1.3	1 613	1.5	1.5	—
286.9	8.9	1.06	8.9			1 612	1.7	1.6	2.1

adsorption time, the absorption band of free Si—OH groups at $3\,736\text{--}3\,743\text{ cm}^{-1}$ disappears completely, and a strong broad band with a maximum at $3\,370\text{ cm}^{-1}$ begins to grow (Fig. 3a, b; curves S). This is accompanied by the appearance of narrow absorption bands at $2\,966$, $2\,917$, $2\,893$ and $2\,854\text{ cm}^{-1}$, corresponding to the stretching vibrations of the dioxane methylene groups. Their intensity, similarly as the intensity of the band at $3\,370\text{ cm}^{-1}$, does not practically change during further dioxane adsorption. These spectral changes are independent of the temperature at which the porous glass has been dehydrated. After dioxane adsorption, the sample dehydrated at 350°C differs from that dehydrated at 220°C only by a somewhat increased intensity of the band at $3\,370\text{ cm}^{-1}$ (see Fig. 3a, b).

In the range of OH stretching vibrations, the infrared spectra of rehydrated porous glass are very similar to the spectra after dioxane adsorption. The spectral changes accompanying water and dioxane adsorption differ profoundly in the rate of their appearance. Whereas during dioxane adsorption the mentioned changes in the range of OH stretching vibrations occur almost immediately, during water adsorption they are relatively slowly established (see Fig. 1a and 3). Thus dioxane adsorption on porous glass appears to proceed much more quickly than would

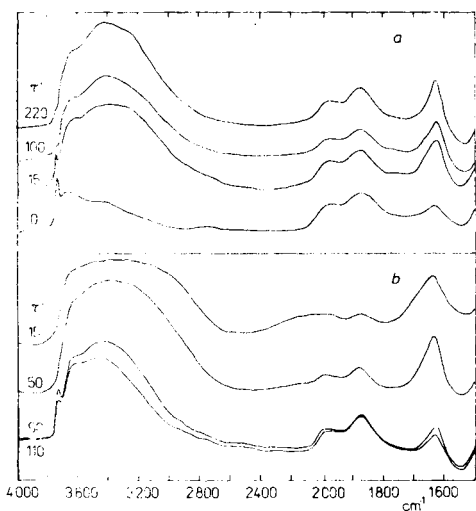


FIG. 1

Time course of the rehydration (τ' , min) of porous glass (pore diameter, d , 11.6 nm) dehydrated at 350°C (a), time course of the dehydration (τ , min) of the same sample hydrated at 97% rel. humidity (b). Lower spectra in the Fig. 1a and 1b: dehydrated samples (curves D)

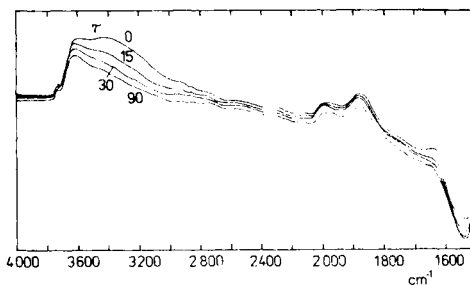


FIG. 2

Time course of the dehydration (τ , min) of porous glass ($d = 53.0\text{ nm}$) hydrated at 97% rel. humidity

correspond to the difference in vapour tensions of dioxane at 25°C ($p = 5.25$ kPa) and water ($p = 3.17$ kPa) (ref.¹²).

Hydrophobization of porous glasses by trimethylchlorosilane is accompanied by irreversible changes in the IR spectra of these materials, as shown in Fig. 4. The absorption band of free Si—OH groups at 3 736–3 743 cm^{-1} disappears completely, with a narrow absorption band appearing at 2 963 cm^{-1} , corresponding to C—H stretching vibrations in —Si(CH₃)₃ (TMS) groups. The absorbance of the TMS band is proportional to the absorbance of the band of free Si—OH groups in the original non-silylated porous glasses, i.e. it decreases with increasing pore size. On the contrary, silylation was not observed to be accompanied by appreciable changes in the intensities of absorption bands of hydrogen-bonded surface silanol groups at 3 500–3 550 cm^{-1} . The changes accompanying silylation of porous glasses dehydrated at 350°C are qualitatively equal to those observed with glasses dehydrated at 220°C. Only the absorbance of the band of TMS groups at 2 963 cm^{-1} is higher, corresponding to the higher absorbance of the band of free Si—OH groups in these samples prior to their silylation.

Hydration of silylated mesoporous glasses leads to a pronounced decrease in the intensity of the ν_2 band, as compared to the original non-silylated samples, corresponding to a decrease in water adsorption by 1–2 orders. On the other hand, with macroporous glasses, silylation was not observed to be accompanied by a systematic decrease in water adsorption (Table II). By deuteration of both the original and of the silylated porous glass sample it was established that all types of silanol

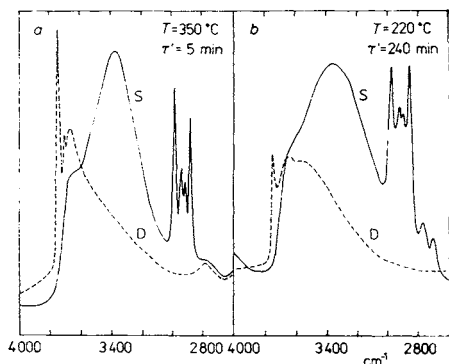


FIG. 3

Comparison of IR spectra of porous glass ($d = 11.6$ nm) dehydrated (curve D) and after 1,4-dioxane adsorption (curve S); T temperature of dehydration, τ' time of adsorption

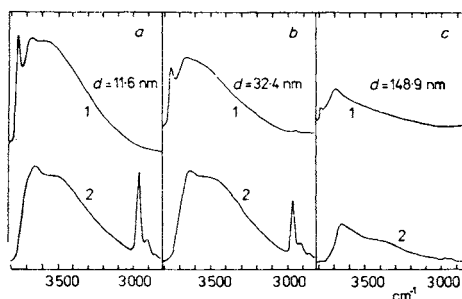


FIG. 4

IR spectra of porous glasses of various porosity dehydrated at 220°C (d pore diameter): 1 original porous glass samples, 2 samples silylated at 220°C

groups undergo isotopic exchange. Spectral changes accompanying deuteration were most rapid in the range of surface Si—OH or Si—OD groups, i.e. at $3\,736$ and $2\,760\text{ cm}^{-1}$, respectively (free silanols) and at $3\,500$ and $2\,550\text{ cm}^{-1}$ (hydrogen-bonded silanols). Deuteration of the sample was further accompanied by a slow decrease in the absorbance of the band of internal Si—OH groups at $3\,670$ to $3\,650\text{ cm}^{-1}$, and by the appearance of the Si—OD band at $2\,680$ – $2\,690\text{ cm}^{-1}$ (Fig. 5). After 15 min of exposure, the H-bonded surface Si—OH groups absorbing at $3\,500\text{ cm}^{-1}$ are fully deuterated in both types of samples. The deuteration of the silylated mesoporous glass is only a little slower than that of the original non-silylated sample of equal porosity (Fig. 5).

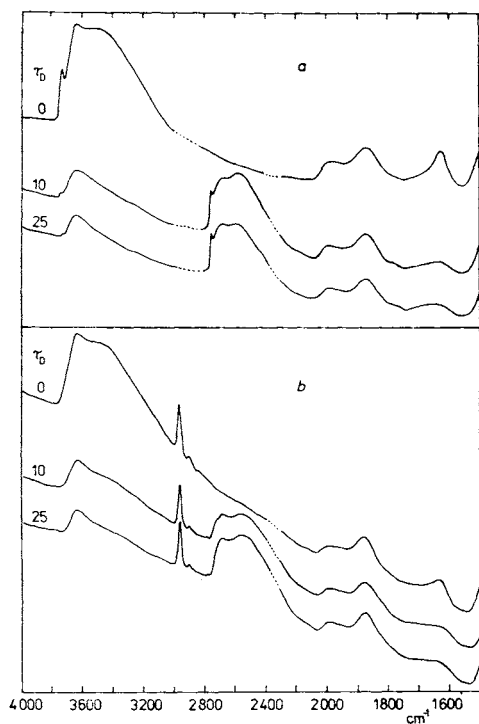


FIG. 5
Time course of deuteration (τ_D , min) of the porous glass with pore diameter 11.6 nm after dehydration at 220°C (a) and after silylation at 220°C (b)

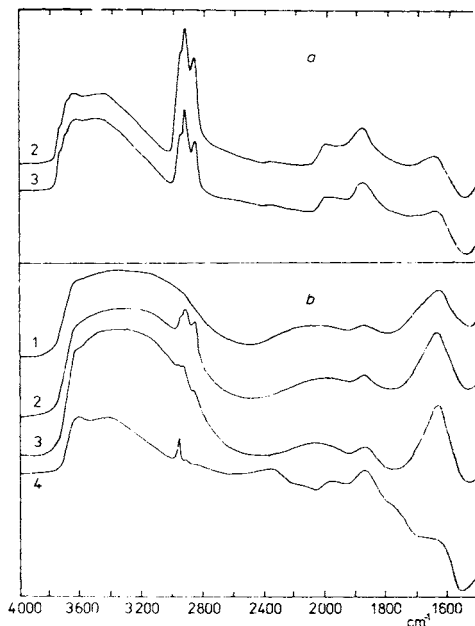


FIG. 6
IR spectra of hydrophobized porous glass ($d = 11.6\text{ nm}$) (a) and after hydrophobization hydrated at 97% rel. humidity (b): 1 without hydrophobization, 2 and 3 hydrophobization with 20% or 3% Nujol, respectively, 4 hydrophobization by silylation

Reversible hydrophobization of porous glasses by Nujol is accompanied in IR spectra by the appearance of absorption bands at 2 980, 2 925 and 2 860 cm^{-1} , corresponding to the absorption of the aliphatic groups of Nujol. The range of OH stretching vibrations exhibits, besides the absorption bands at 3 640, 3 500 and 3 735 cm^{-1} corresponding to internal, surface H-bonded and free silanols, a new shoulder corresponding to the absorption band at 3 695 cm^{-1} (Fig. 6a). Hydration of porous glass hydrophobized by Nujol is accompanied by the appearance of strong absorption bands at 3 400 and 1 636 cm^{-1} , corresponding to adsorbed water. Even at high contents of adsorbed Nujol, the intensity of these bands is comparable to that of water bands observed during hydration of the original sample of porous glass. The strong water absorption bands of mesoporous glass hydrophobized by Nujol indicate a high content of water in these materials. The intensity growth of water absorption bands in reversibly hydrophobized porous glasses is accompanied by the complete disappearance of the bands at 3 735 and 3 695 cm^{-1} (Fig. 6b).

DISCUSSION

The decrease in absorbance of bands in the range of the vibrations of hydrogen-bonded surface and internal Si—OH groups with increasing temperature of porous glass dehydration is caused by dehydroxylation of these groups and by the removal of traces of adsorbed water⁷. The less familiar phenomenon, i.e. the increase in absorbance of free silanol groups at dehydration temperatures above 300°C, can be also explained as a consequence of dehydroxylation, in the course of which a part of the H-bonded surface Si—OH groups are transformed into free ones. Samples of porous glass with various contents of hydrogen-bonded and free surface Si—OH groups, of equal porosity (11.6 nm) were used in studies of dioxane interaction with porous glasses.

The disappearance of the band of free Si—OH groups at 3 736–3 743 cm^{-1} and the appearance of the strong absorption band at 3 370 cm^{-1} during dioxane adsorption in porous glasses can be explained by the formation of hydrogen bonds in which the dioxane ether groups act as proton acceptors¹³. (Isolated Si—OH groups serving as proton donors in these bonds, will further be designated as Si—OH···dioxane.) The interaction between hydrogen-bonded surface Si—OH groups and dioxane cannot be directly proved from IR spectra. The absorption band of these groups at 3 550 cm^{-1} is completely overlapped by a strong band of Si—OH···dioxane groups at 3 370 cm^{-1} . Nevertheless the interaction between surface H-bonded Si—OH groups and dioxane could be estimated indirectly from the difference between IR spectra of porous glass dehydrated at various temperatures, i.e. at 220 and 350°C, prior to dioxane adsorption.

With porous glass dehydrated at 220°C, the absorption intensity at 3 370 cm^{-1} is enhanced by the presence of the band of vicinal Si—OH groups at 3 550 cm^{-1}

(Fig. 3b). After subtraction of the vicinal silanol band, the absorbance of the Si—OH...dioxane band at $3\,370\text{ cm}^{-1}$ is about two times lower as compared to the sample of equal porosity dehydrated at 350°C . This ratio is in good agreement with the absorbance ratio of the band of free Si—OH groups at $3\,736\text{--}3\,743\text{ cm}^{-1}$. In a porous glass sample ($d = 11.6\text{ nm}$) after dehydration at 220°C , the intensity of this band is 1.8 times lower than after dehydration at 350°C (Fig. 3a, b). Based on this comparison we conclude that:

a) the absorbance of Si—OH groups interacting by hydrogen bonds with dioxane depends only on the contents of isolated Si—OH groups;

b) during dioxane adsorption, the absorbance of vicinal (hydrogen-bonded) Si—OH groups may be regarded as approximately constant.

The statements a) and b) may be summarized to conclude that hydrogen bonds between surface silanol groups and dioxane are probably formed with isolated Si—OH groups. Even in the presence of adsorbed dioxane molecules, vicinal surface Si—OH groups interact only by means of mutual hydrogen bonds Si—OH...O(H)—Si.

Adsorption of dioxane on porous glass is accompanied by similar spectral changes as adsorption of water. In both cases the absorption band of free Si—OH groups disappears, and a strong band appears around $3\,400\text{ cm}^{-1}$, corresponding to strong hydrogen bond formation. We assume that both during dioxane and water adsorption, proton-donating hydrogen bonds are only formed by isolated Si—OH groups.

To complete our notions on the mode of interaction of porous glasses with polar solvents, we have studied the hydration of porous glasses hydrophobized by chemisorption of trimethylchlorosilane (silylation) or by physical Nujol adsorption. These samples are characterized by the presence of a hydrophobic layer of non-polar aliphatic groups, partly or completely separating the hydrophilic surface of the adsorbent from the adsorbing water molecules.

Silylation of porous glasses leads to a selective removal of free Si—OH groups^{14,15}, also shown by our results. It has been known that the amount of adsorbed water is substantially reduced by silylation (see Table II). This has been thought to result from the shielding of the porous glass surface by the voluminous —Si(CH₃)₃ groups, preventing contact of adsorbed water molecules with unreacted silanol groups for steric reasons^{7,16}. We tried to check this assumption both by spectroscopic studies of water adsorption on glasses hydrophobized by trimethylchlorosilane or by Nujol, and by studies of the course of deuteration of silylated glasses. Hydration of porous glasses hydrophobized by Nujol is accompanied by a complete disappearance of both absorption bands of free Si—OH groups, at $3\,735$ and $3\,695\text{ cm}^{-1}$ (Fig. 6b). The band at $3\,735\text{ cm}^{-1}$ corresponds to free Si—OH groups without any kind of interaction, and its disappearance is a normal effect during porous glass hydration. The band at $3\,695\text{ cm}^{-1}$ corresponds to isolated Si—OH groups, the wavenumber of which is reduced due to the increased dielectric constant of the medium in the presence of Nujol¹⁷. We explain the disappearance

of this band during porous glass hydration by the dynamic character of the complex formed by interaction of Si—OH groups with the non-polar aliphatic groups of Nujol. We assume this complex to be of the "collision complex" type, of very short life-time, practically limited to the duration of the collision between the polar and non-polar, or weakly polar group¹⁸. The consequence of this is that at the intervals between the collisions of the aliphatic groups of Nujol with the free Si—OH groups, these silanol groups are free of any interaction. We assume that in this state they are spatially accessible for the polar molecules of adsorbed water with which they interact by means of hydrogen bonds. The formation of these bonds is manifested by the gradual disappearance of both absorption bands of the isolated Si—OH groups at 3 735 and 3 695 cm^{-1} in the course of hydration (Fig. 6a).

Deuteration of silylated mesoporous glass has shown that the rate of isotopic exchange $\text{OH} \leftrightarrow \text{OD}$ is comparable to that of the non-silylated (original) glass sample. From this we conclude that the interaction of adsorbed water with surface hydrogen-bonded Si—OH groups remains unaffected by the layer of voluminous hydrophobic $-\text{Si}(\text{CH}_3)_3$ groups (compare Fig. 5a, b).

Studies of water adsorption on porous glass hydrophobized by Nujol as well as deuteration studies of silylated porous glasses indicate that the presence of the hydrophobic groups themselves evidently is not the cause of the lowering of hygroscopicity of silylated porous glasses. We assume that the low contents of water adsorbed in these materials is primarily the consequence of the consumption of free Si—OH groups by silylation.

The wavenumbers of the absorption bands of bending vibrations of water adsorbed in porous glasses at 97% rel. humidity (1 612–1 638 cm^{-1}) are lower than those of liquid water (1 645 cm^{-1}) (ref.⁶). For mesoporous glasses with pore diameters $d < 10$ nm, the mean shift of the ν_2 band amounts to only 7–10 cm^{-1} , for macroporous glasses to 24–33 cm^{-1} , as compared to liquid water (Table II). We explain the wavenumber shifts of the ν_2 band in macroporous glasses as a manifestation of weakened hydrogen bonds in the adsorbed water, as compared with the liquid state. On the other hand, for mesoporous glasses (with the exception of the sample with $d = 8.5$ nm) the degree of association may be assumed to be equal to that of liquid water.

The size of the pore radius, r , at which capillary condensation occurs at a relative tension of water vapours p/p_0 , for a general shape of the capillary meniscus is given by the relation¹⁹

$$\frac{k}{\ln p/p_0} \leq r \leq \frac{2k}{\ln p/p_0} \quad (3)$$

The expression at the left side of the inequality (3) corresponds to a spherical shape of the meniscus, the expression at its right side to a cylindrical meniscus. For a zero

wetting angle between the porous glass surface and the level of the capillary condensate, k is defined by the relation

$$k = -\sigma M/RT, \quad (4)$$

where M is the molar mass of water, σ its surface tension, R the universal gas constant and T the absolute temperature. When the values of the relative vapour tension of water, at which the porous glasses have been hydrated, are substituted into this equation, then for p/p_0 the maximum pore diameter fulfilling the condition for capillary condensation lies in the range of $2r = 35 - 70$ nm; this corresponds roughly to the maximum pore diameter of mesoporous glasses (≈ 50 nm). For porous glass hydration at 56% rel. humidity, relation (3) predicts that the maximum pore diameter suitable for capillary condensation lies at $d = 1 - 2$ nm. This value is substantially lower than the smallest mean pore size of the measured samples (8.5 nm). In view of the narrow pore size distribution, the existence of pores with $d \leq 2$ nm is very improbable. This means that at 56% rel. humidity, conditions for capillary condensation are not fulfilled in any of the measured porous glass samples. Nevertheless, for mesoporous glasses hydrated at this rel. humidity, the wavenumbers of the ν_2 bands are relatively high (Table II), corresponding to a fairly high degree of association.

The high degree of water association in mesoporous glasses hydrated at low relative humidity can be explained by an inhomogeneous distribution of water molecules at the internal surface of these compounds. We assume that during hydration small clusters of water molecules are formed at some places on the pore surface, and that the shape of these clusters is deformed by adhesion forces. This results in enhanced degree of water association in these clusters by means of hydrogen bonds, as indicated by the enhanced wavenumber of the ν_2 band. Such clusters of water molecules can only be formed in sufficiently small pores, i.e. in mesoporous glasses: The high negative curvature of the pore surface in this case reduces the value of the positive curvature of the cluster surface and thus reduces the vapour tension of the water molecules in these clusters. For macroporous glasses, with lower surface curvature, we assume water to be adsorbed in a uniform layer. The thickness of this layer, and the degree of water association in these materials is lower than in mesoporous glasses. This is indicated by the low contents of adsorbed water and by the low wavenumber of the ν_2 band in spectra of macroporous glasses (Table II).

Adsorption of water vapour on mesoporous glass is accompanied by a relatively slow reduction of the absorption intensity of free Si—OH groups (Fig. 1). This course of spectral changes during hydration is explained so that even before the occupation of all free Si—OH groups by water molecules, H—O—H...OH₂ bonds begin to be formed. In this way, water clusters are formed in the vicinity of those Si—OH groups which were the first to interact with water; formation of these clusters competes with the hydration of other (unoccupied) Si—OH groups. In this way the

course of water adsorption differs considerably from the very rapid rate of dioxane sorption (Fig. 3), where a quick, practically simultaneous occupation of all free Si—OH groups is assumed.

The idea of clusters formation during water adsorption, localized at some places of the pore surface, is in good agreement with the observed, relatively high wave-number of the ν_2 band of mesoporous glasses; this value changes but little with increasing water contents. We assume that the cluster size grows in the course of water adsorption, simultaneously with the generation of Si—OH \cdots H₂O bonds on all the remaining (originally unoccupied) isolated Si—OH groups. In consequence of this process, the pores are then gradually filled by the capillary condensate. After the isolated Si—OH groups have been removed, i.e. only in the presence of vicinal (hydrogen-bonded) Si—OH groups, capillary condensation does not take place, as indicated by the low amount of water adsorbed in silylated porous glasses (Table II). This is probably caused by the low tendency to hydrogen bond formation between these groups and molecules of adsorbed water, or polar oxygen containing molecules in general.

CONCLUSIONS

Spectroscopic measurements indicate that in the course of water adsorption in porous glasses, strong hydrogen bonds are gradually formed between water molecules and free surface Si—OH groups. In glasses with pore diameters less than 50 nm, i.e. in mesoporous glasses³, this process is accompanied by a simultaneous formation of clusters of water molecules, with a high degree of association. The formation of hydrogen bonds between hydrogen-bonded surface Si—OH groups and the studied polar molecules, i.e. water and dioxane, was not confirmed. We assume that the formation of clusters at the surface of mesoporous glasses precedes capillary condensation during their hydration in the vapour phase. Further findings obtained by IR spectroscopic studies of porous glasses concern the phase structure of adsorbed water. Our measurements indicate that the degree of water association in mesoporous glasses is near to the degree of association in liquid water, and depends little on the water contents in the glass. On the other hand, in porous glasses with pore diameters larger than 50 nm, i.e., in macroporous glasses, the association degree of adsorbed water approaches the state of water molecules in the gas phase.

Spectral changes observed during hydration of porous glasses as well defined model compounds may serve as a basis for our understanding of the phenomena manifested upon hydration of natural silicate materials.

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