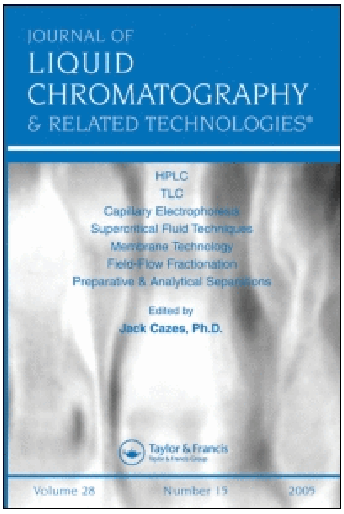

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A Geometrical Model for Chemically Bonded TMS and PDS Phases

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A GEOMETRICAL MODEL FOR CHEMICALLY BONDED TMS AND PDS PHASES

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ABSTRACT

A geometrical model is developed for monomeric TMS and PDS phases that are chemically bonded to silica. Using experimental data for maximum surface coverage and considering amorphous silica as a collection of distorted crystals, we calculate that each nm^2 of the silica surface contains 2.3 modified hydroxyl groups, 1.3 free hydroxyl groups and 0.6 pairs of bonded hydroxyl groups, respectively. From the dimensions of the silane molecule it is concluded that for maximum coverage the TMS and PDS molecules are rigidly attached to the silica surface with an Si-O-Si bond angle between 120 and 140 degrees. The unreacted hydroxyl groups are not completely screened but will be quite inaccessible on either phase. Very little free surface area remains on the silica surface.

INTRODUCTION

The state of the art of chemically bonded stationary phases for liquid chromatography has been described in two recent reviews. In his general survey of stationary phases for HPLC Majors [1] concludes that for liquid-liquid chromatography physically coated stationary phases appear to have been all but replaced by chemically bonded phases. Colin and Guiochon[2] note that despite their widespread use in reversed-phase liquid chromatography the structure and the retention mechanism of chemically bonded phases are still a matter of dispute. We agree with their conclusion that "the most important reason for the current controversy regarding the structure and properties of bonded phases and especially the retention mechanism arises from the great difficulties encountered in preparing batches of silica gels and modified silica gels which are reproducible or even repeatable".

To improve our insight it is, therefore, a prerequisite to possess well-defined bonded phases for which the surface coverage - expressed as the number of modified hydroxyl groups [3] - can be calculated with a minimum of additional assumptions. In this respect alkoxysilanes or dichloro and trichlorosilanes are less suitable, because they can react with one or two hydroxylgroups and are subject to polymerization reactions. Such problems are avoided if we use monochlorosilanes, such as trimethylchlorosilane (TMS) or phenyldimethylchlorosilane (PDS). Even then two additional data are needed to convert the carbon content of the modified silica to the number of hydroxylgroups removed, i.e. the specific surface area of the packing material and the surface density of hydroxyl groups originally present. Literature data, confirmed in the present study agree that modification of hydroxyl groups is never complete [2, 3], so that the chromatographic activity of remaining hydroxyl groups remains debatable. Chromatographic retention data can be useful, but careful experiments are required to differentiate between the influence of the mobile phase, the activity of unmodified hydroxyl groups and the properties of the chemically bonded phase. Such experiments will be reported in a following paper [4], which also describes the preparation of well-defined monomeric phases.

In this study we explore another approach. Except for a non-validated statement by Unger and coworkers [3,5] that the maximum coverage by TMS agrees with values calculated from molecular sizes, the molecular geometry of chemically bonded phases appears to have been ignored. In this investigation we shall present a [illegible]rical model based on molecular dimensions, that provides us with a better insight into the structure of the bonded phase and the screening of remaining hydroxyl groups.

THE STRUCTURE OF SILICA

There are two basic types of silica: crystalline and amorphous, the latter being exclusively used in chromatography. Both types possess the same structural unit consisting of siliconoxide tetrahedrons. The essential difference between either type is the orientation of the tetrahedrons in space. The structure of crystalline silica consists of a three dimensional network of parallel planes of similar units, whereas in the amorphous silica the parallel planes are missing although the three dimensional structure persists [6].

The structure of the various crystalline forms of silica is well-known from X-ray diffraction studies. Some relevant date are collected in Table 1. Three main crystalline forms can be distinguished: quartz, tridymite and cristobalite, each existing in several modifications [7, 8]. Although these main types are stable over well defined temperature ranges (quartz up to 870° C, tridymite between 870 and 1470° C and cristobalite above 1470° C), they are not readily interconvertible, as is shown by the fact that all three are found as minerals, though tridymite and cristobalite are rare in comparison with quartz. The transition points of the α and β modifications of tridymite and cristobalite are at relatively low temperatures, 120 - 160° and 200 - 275° C, respectively. The fact that these transitions can be studied at temperatures at which the forms are metastable is a further indication of the difficulty of converting one of the three varieties of silica into another [9]. Consequently, all crystalline forms can exist under

TABLE 1

MODIFICATIONS OF SILICA*)

SiO_2-form	crystal system	Si-O-Si bond angle	specific gravity (g/cm^3) [29]	molar volume (cm^3) [29]	Si atoms per nm^2	number of hydroxyls per nm^2	
						calculated from density	literature data
α-quartz	hexagonal	142° [9]	2.65	22.69			
β-quartz	hexagonal	150° [14]	2.53	23.72	8.6	4.3	4.3 [11,41]
α-tridymite	rhombic	--	2.26	26.59			
β_1-tridymite	hexagonal	180° [8]	2.19	27.41	7.8	3.9	4.6 [11-13]
β_2-tridymite	hexagonal	180° [8]	2.19	27.41			
α-cristobalite	tetragonal	150° [9]	2.33	25.74			
β-cristobalite	cubic	180° [14,37]	2.19	27.38	7.8	7.8	7.9 [11-13]
anhydrous nonporous	amorphous	--	2.2**)	27.3			
anhydrous porous	amorphous	--	1.9***)	31.6	7.1	≥ 3.6	4.8

*) the references are presented between square brackets

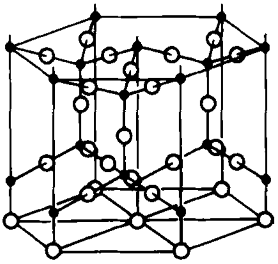
) ref. 38 and 39 *) ref. 40

ordinary conditions encountered in chromatographic columns. In turn, each of these crystals can be considered as a starting point to formulate a model for the amorphous silica used in chromatography.

Indeed, by nature of its amorphous character, the silicas of chromatographic interest cannot be analysed by X-ray diffraction or by surface techniques, such as ESCA. Consequently, several authors consider the structure of amorphous silica as a distorted crystal. Stöber [10] took the quartz structure as a starting point, whereas Iler [11], Hockey and coworkers [12, 13] and Boksânyi et al. [14] argue that amorphous silica should closely resemble the β-modifications of cristobalite or tridymite. According to the data in Table 1 there is a difference in density and Si-O-Si bond angle between quartz on the one hand and β-tridymite and β-cristobalite on the other hand.

For the present study it is more important to note the difference between the three crystalline forms with respect to the number of free hydroxyl groups at the surface. Obviously, this number depends upon the crystal face considered, but it is appreciably higher for β-cristobalite than for quartz or β-tridymite. This is due to the fact that the outer surface silicon atoms in β-cristobalite are bound to two oxygen atoms and hence possess two hydroxyl groups, whereas in quartz and β-tridymite the surface silicon atoms are bound to three oxygen atoms and hence possess only one hydroxyl group. Now in all crystalline forms the surface layer consists alternatingly of a true surface silicon atom with one or two oxygen bonds ruptured and a slightly lower situated silicon atom connected to four oxygen atoms (compare fig. 1). Consequently, in β-cristobalite the number of free hydroxyl groups is equal to the number of silicon atoms in the surface layer, whereas in quartz and β-tridymite the number of hydroxyl groups is equal to half the number of silicon atoms in the surface layer.

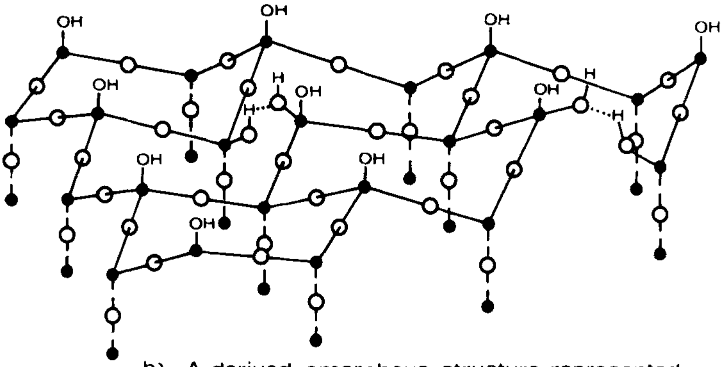
Given the ordered structure of a crystal, the number of hydroxyl groups can be readily calculated for any crystal face. Some



a) The hexagonal crystal structure of β-tridymite

O = oxygen atom

● = silicon atom



b) A derived amorphous structure represented as a distorted β-tridymite

FIGURE 1

indicative data are included in Table 1. However, such figures are of little use for amorphous silica, where the regular structure is lost. In addition to the widely spaced free hydroxyl groups found at the crystal surface amorphous silica also contains more closely spaced hydroxyl groups. Since the distance between the latter is less than 0.3 nm, they can give rise to hydrogen bonds, as is clear from the infrared spectrum of amorphous silica [15 - 21].

However, neither the total surface density of hydroxyl groups nor the fractional contribution of free and bound hydroxyl groups has been definitely established. One reason for this is the presence of physically adsorbed water molecules. The temperature at which physically adsorbed water is completely removed has been reported between 115 [11] and 200° C [20], but most authors agree that prolonged heating at 150 - 200° C in vacuo effectively removes physically adsorbed water [16 - 22]. More recently Cortés [23] and Morariu [24] established that the upper value is correct.

The estimates for the remaining hydroxyl density range from a low 3.6 nm^{-2} to a high 9.5 nm^{-2}, depending upon the measurement technique and the temperature applied to the silica. With infrared spectrometry and thermogravimetric analysis the sum of surface and bulk hydroxyl groups is determined [11, 25], whereas deuterium exchange or surface reactions measure only the surface hydroxyls. In this study we adopt a value of 4.8 nm^{-2} for the surface density of hydroxyl groups remaining after removal of physically adsorbed water at 200° C. The value of 4.8 nm^{-2} appears to be well validated by studies of several authors [16, 17, 20, 22, 26].

The differentiation between free and bound hydroxyl groups is of interest, because there is some conflict of opinion about their respective reactivity. Snyder [15] assumes that chlorosilanes react preferentially with bound hydroxyl groups, whereas Kiselev [20, 21] argues that the free hydroxyl groups are the more reactive, which opinion is shared by Hertl [27] and by Armistead et al. [28].

A differentiation between free and bound hydroxyls might be based upon the observed decrease of the total hydroxyl content with increased heating of the silica. Changes in the infrared spectrum indicate that hydrogen bonded hydroxyls are released sooner than the free hydroxyl groups. Kiselev [18] uses this argument to conclude from the decrease of the hydroxyl content between 200 and 400° C that there are 2.2 bound hydroxyl groups per nm^2, so that for a total surface density of 4.8 nm^{-2} there must be 2.6 free hydroxyl groups per nm^2. Armistead et al. [13] make the distinction after heating at 450° C through reaction with $Si(CH_3)_2Cl_2$, $TiCl_4$ and BCl_3 with surface hydroxyl groups and report more interacting hydroxyl groups (3.2 nm^{-2}) and less single surface hydroxyls (1.4 nm^{-2}) for a total surface density of 4.6 nm^{-2}. It seems to us that either temperature is rather arbitrary. Observation of the data [20, 23, 24] reveals that the weight of amorphous silica decreases quite gradually when it is heated from 200 to 1000° C. This indicates that the temperature ranges where free and bound hydroxyl groups are released overlap strongly, and there is no well-defined "transition"-temperature where all bonded hydroxyls have been removed and all free hydroxyl groups have remained.

For this reason we have adopted a structural model for amorphous silica to differentiate between free and bound hydroxyl groups. This model considers amorphous silica to be a grossly distorted crystal. The distortion is due to the rupture of an appreciable number of silicon-oxygen bonds throughout the crystal. This is illustrated in fig. 1 for the example of β-tridymite. Each ruptured bond gives rise to two additional hydroxyl groups that are separated to such an extent that they form a hydrogen bond. Consequently, the number of free hydroxyls remains equal to that found in the corresponding crystal, whereas the number of bound hydroxyls is twice the number of ruptured Si-O bonds. The bond ruptures will also increase the volume of amorphous silica as evidenced by its lower density in comparison to crystalline forms (table 1). As a result the geometry of the substance is distorted to such an extent that its surface reflects a collection of different crystal faces. In other words amorphous silica is considered to consist of randomly orientated crystals with an uneven surface.

This allows us to equate the surface layer of amorphous silica to an average surface layer of the corresponding crystal. In turn, the number density of silicon atoms in this surface layer can be calculated as

$$\text{surface density Si} = (N_A/V_m)^{2/3} \tag{1}$$

$$= (6.023 \times 10^{23}\rho/60.1)^{2/3} \times 10^{-14}\ \text{nm}^{-2}$$

where N_A is Avogadro's number, V_m is the molar volume of SiO_2 and ρ is the density of silica in g/cm^3. Results from equation (1) are entered in Table 1.

From these data the surface density of free hydroxyls is readily derived if we recall that there is one hydroxyl group for every silicon atom in cristobalite, but one for every second silicon atom in quartz and tridymite. The surface densities of hydroxyl groups calculated in this way are in good agreement with the exact surface densities calculated for a well-defined crystal face, exept for β-tridymite. This difference can partly be attributed to the fact that tridymite's crystal form never consists of pure SiO_2 [7, 8] and the calculations are based on X-ray crystallographic data of minerals [29], table 1.

Obviously, however, the high surface density predicted for β-cristobalite (7,8 nm^{-2}) makes it unlikely that amorphous silica resembles this type of crystal, since the total surface density of hydroxyl groups in amorphous silica is only 4.8 nm^{-2}. It is not possible to differentiate between quartz and tridymite on this basis, although we agree with other authors [12, 30], that the latter provides a more probable model for amorphous silica.

In either case we conclude that in amorphous silica the number of free hydroxyl groups is equal to the number of silica atoms in the surface layer. Allowing for the lower density of amorphous silica we calculate its surface density of free hydroxyl groups from equation (1) as 3.6 nm^{-2}. Consequently, if the total surface density of hydroxyl groups is 4.8 nm^{-2}, we must expect 1.2 bound hydroxyl groups per nm^2, resulting from 0.6 ruptured bonds per nm^2 surface layer.

These date should be compared to the maximum coverage obtained when the silica surface is modified with a well-defined monomeric phase. As will be described elsewhere [4] we obtained for LiChrosorb SI100 with an average surface area of 299 m^2/g a maximum coverage of 2.3 TMS molecules per nm^2 and 2.1 PDS molecules per nm^2. Extensive post treatment with excess TMS did not change the carbon content and the chromatographic retention characteristics of either bonded phase. The value found for TMS agrees fairly well with the values of 2.4 and 2.7 nm^{-2} reported by Unger [3], which are the highest reported in the literature [2]. On the other hand our value for PDS is significantly larger than the value of 1.6 nm^{-2} reported by Unger [3] and Kirkland [31].

Comparing the maximum bonded phase coverage with the surface densities of free and bound hydroxyl groups mentioned above, we conclude that the former must be the more reactive towards chlorosilane. Indeed, if the silane molecule reacted only with bound hydroxyl groups, as argued by Snyder [15], the maximum surface coverage could not exceed 0.6 silane groups per nm^2, which is much lower than the experimental values realized for either TMS or PDS. If, on the other hand, the silane molecule reacts with all free hydroxyl groups, we would expect a maximum coverage of 3.6 silane groups per nm^2, which is nearly 40% larger than observed experimentally. However,this argument completely ignores the geometry of the bonded phase molecule. In the next section we consider a geometrical model for the chemically bonded TMS phase that accounts for a silica surface where one nm^2 contains 1.2 bound hydroxyl groups, 2.3 chemically modified hydroxyl groups and 1.3 remaining free hydroxyl groups. For PDS the figures are 1.2 bound, 2.1 modified and 1.5 unmodified free groups, respectively.

GEOMETRY OF THE BONDED PHASE

In order to calculate the dimensions of the silane molecules bonded to the silica surface, we need data on the size of the atoms, the bond length between adjacent atoms and the angle between two successive bonds. Although the atoms in crystalline silica are described by ionic radii, the atoms of the covalent silane molecule must be measured by their Van der Waals radii. The data collected in Table 2 for the atomic radii and the covalent bond lengths represent the minimum values reported in the literature [29, 32-34]. The bond angles in the silane molecule offer no problem, but the angle of the Si-O-Si bond through which the molecule is attached to the silica surface is less certain.

The data in Table 1 show that the Si-O-Si angle in the crystal lattice varies from 142° for α-quartz to 180° for β-tridymite. On the other hand, for some linear and cyclic polysiloxane molecules, this angle is reported as 130° for hexamethyldisiloxane [9, 35], 142° for Si_4O_4 [9] and 175° for hexachlorodisiloxane [35]. Finally, the angle between two typical covalent oxygen bonds in alcohols and ethers is only 110° [35] and a comparable low value (113°) is also reported for the Si-O-H bond angle of free hydroxyl groups at the silica surface [36]. In view of this wide variation of possible Si-O-Si bond angles, we have carried out the geometrical calculations for several different angles between 110 and 180°. The results are presented in Table 3 for TMS and in Table 4

TABLE 2

Van der Waals radii (nm)	Covalent bonds (nm)
O-atom = 0.140	O-Si = 0.183
Si = 0.195	C-Si = 0.189
H = 0.100	C-C (benzene, experimental)
CH_3-group = 0.200	= 0.138
thickness aromatic	=C-H = 0.106
ring = 0.355	

TABLE 3

THE CROSS-SECTIONAL AREAS OF THE TMS-PHASE (in nm^2)

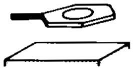
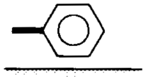
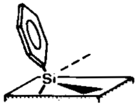
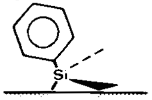
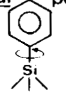
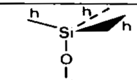
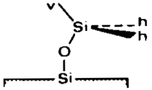
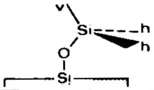
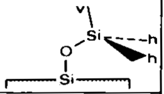
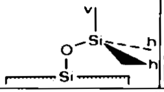
Si-O-Si angle	rigid position of the TMS-group	rotation around the ⁝Si–↻–O bond of the TMS-group
180^o	$0.335^{*)}$	0.449
150^o	0.325	0.648
140^o	0.308	0.709
120^o	0.287	0.715
110^o	0.281	0.625

*) Kiselev [18] used 0.348 nm^2

for PDS and are expressed as the projections of the molecular cross-section onto the silica surface.

Now for TMS the maximum surface density realized is 2.3 groups per nm^2, so that in this situation each TMS molecule covers an average area of 0.43 nm^2. If the TMS molecules completely cover the surface and are also rigidly attached to the surface, this value would also represent the actual cross-section of the molecule. If, however, the TMS molecules are free to rotate around the Si-O bond through which the silane molecule is attached to the surface, then the actual cross-section of the molecule must be smaller to allow this rotation. The exact value depends upon the number of closest neighbours. If we assume that the amorphous silica resembles a distorted β-tridymite crystal, then fig. 1 shows that there can be six neighbouring TMS molecules. In that case the circular area available to each TMS molecule would be only 0.39 nm^2.

TABLE 4
The cross-sectional areas of the PDS-phase, nm^2

Si-O-Si angle	position of the PDS-group with regard to the silica surface *)	position of the phenyl-group with regard to the silica surface "horizontal"		"vertical"		free rotation of the phenyl-group in "vertical" position
						
		A	**B**	**C**	**D**	**E**
180°		0.544	0.446	–	–	–
150°		0.531	0.427	0.467	0.390	0.497
140°		0.507	for lack of space with the silica surface these positions are impossible	0.417	0.374	0.468
120°				0.324	0.326	0.385
110°				0.281	0.301	0.332

*) v = "vertical" position ; h = "horizontal" position

This value is smaller than any of the cross-sections presented in Table 3 for the freely rotating TMS molecule. Even for a Si-O-Si bond angle of 180° the rotating TMS molecule calculated with minimum values for atomic radii and bond lengths needs 0.45 nm^2, whereas only 0.39 nm^2 is available for a surface density of 2.3 TMS molecules per nm^2. Thus we can conclude that for maximum coverage the TMS molecules are rigidly attached to the silica surface and cannot rotate freely around the Si-O bond to this surface.

A rigid position of the TMS group is possible for all bond angles considered in table 3. Not only is the space actually occupied by each TMS molecule enlarged to 0.43 nm^2, but all calculated cross-sections are significantly reduced. In fact, in this situation we must expect open surface areas between adjacent TMS molecules.

For the PDS phase the situation is much more complex. For Si-O-Si bond angles different from 180° we can distinguish between the situation where the phenyl group is more or less "horizontal" to the silica surface, denoted by "h" in table 4, and the situation where this group points away from the surface, the "vertical" position "v". In addition to this, the phenylring can be parallel (columns A and C) or antiparallel (columns B and D) to the silica surface. Finally column E presents data for a freely rotating phenylring.

Following the same argumentation as for TMS we can calculate the average area available to the PDS molecule in the situation of maximum coverage. The observed surface density of 2.1 PDS groups per nm^2 yields an average area of 0.48 nm^2 for a rigidly attached PDS molecule. This value would be lower if the PDS molecule is allowed to rotate freely around the Si-O bond to the surface, but the data in Table 4 make it clear that this is quite impossible. In fact the available area of 0.48 nm^2 is smaller or only slightly larger than the cross-sections calculated in Table 4 for a "horizontally" orientated phenyl group. Since the data in Table 4 are calculated from minimum values for atomic radii and bond lengths, we consider such a close fit very unlikely, data of column B. Indeed it could only be realized if the PDS molecules are very regularly spread over the silica surface leaving no space for unreacted hydroxyl groups. Consequently, we conclude that for maximum coverage of the PDS phase the phenyl group points away from the silica surface. Moreover, a bond angle of 180° for the Si-O-Si bond is definitely ruled out.

For Si-O-Si bond angles of 140 to 150° only the values in column D are sufficiently smaller than the available area of 0.48 nm^2, so that for such a bond angle the phenyl ring and hence the entire PDS molecule will be in a fixed position with respect to the silica surface. It is only for the smaller Si-O-Si bond angles of 110 to 120° that the calculated cross-sections allow rotation of the phenylring around the Ph-Si bond.

However, even in this situation, the polar nature of the phenyl group certainly forces the group into an energetically favourable fixed position with respect to unreacted surface hydroxyl groups. Such a position will be reached through rotation around the $O\text{-}Si(CH_3)_2Ph$ bond of the silane molecule or around the Si-Ph bond.

In order to establish the position of the PDS molecule more definitely, we return to the TMS-phase. Since large bond angles have been ruled out on the evidence provided for the PDS phase, we consider only Si-O-Si bond angles between 110 and 150°. In that case the cross-section of the TMS molecule is decidedly smaller than the average area of 0.43 nm^2 available with maximum coverage. However, at the actual silica surface there must be room not only for the TMS molecules, but also for unreacted free and bound hydroxyl groups.

Fig. 2a shows that for a Si-O-Si bond angle of 110° the bulky methyl groups actually penetrate the silica surface, so that this bond angle is possible only if there is a dent in the silica surface close to the modified silicon atom. It is easily calculated that the limiting angle where the methyl group just touches a flat

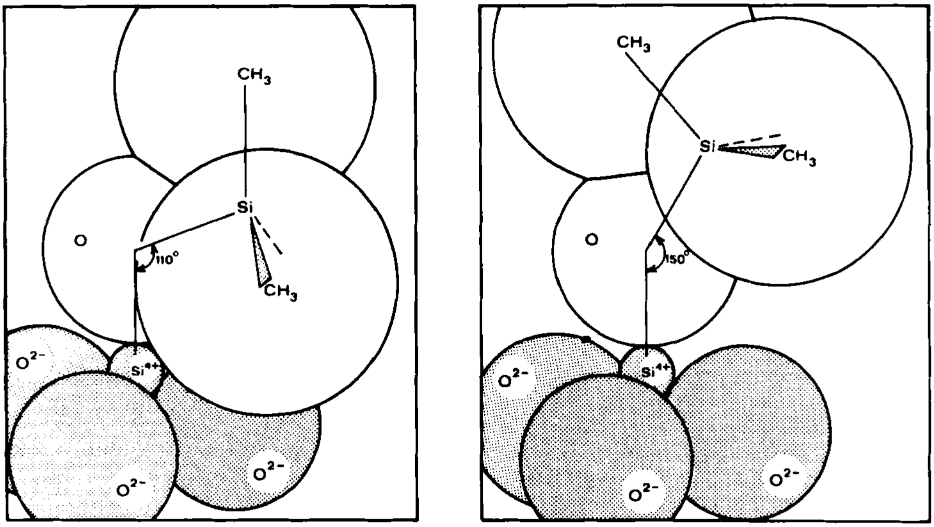


FIGURE 2a FIGURE 2b

Side view of a TMS molecule bonded to the silica surface with a Si-O-Si bond angle of 110° (left) or 150° (right)

shaded ions (with ionic radii) refer to the silica surface : open circles (with van der Waals radii) represent a TMS-molecule located above that surface

silica surface is 120°. Obviously, for Si-O-Si bond angles equal to or smaller than 120° the TMS molecules cannot even partly cover any of the unreacted hydroxyl groups. Note that the same argument holds for the PDS-phase, because the phenyl group as demonstrated above, points away from the silica surface. Fig. 2b shows that for a Si-O-Si bond angle of 150° there is a limited space available between the methyl group and the silica surface under which a free hydroxyl group can partly hide. This would seem to favour a larger bond angle, but the data in Table 3 show that the cross-section of the TMS molecule increases with increasing bond angle. Again, the same is true for the PDS-phase.

The opposite effects of partial screening of hydroxyl groups and increased cross-section of TMS are illustrated more clearly in figures 3 and 4.

At the end of the preceeding section, we have argued that the silica surface contains on every nm^2 2.3 TMS molecules, 1.3 free

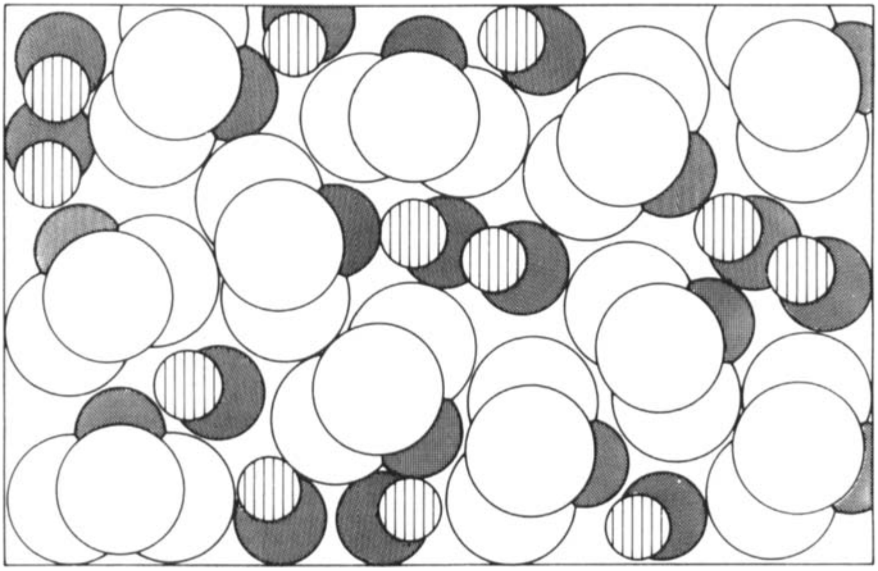


FIGURE 3

Silica surface for maximum TMS-coverage; Si-O-Si bond angle of 110°
circles represent projections of methylgroup (open), oxygen atom (dark shaded) and hydrogen atom (hatched)

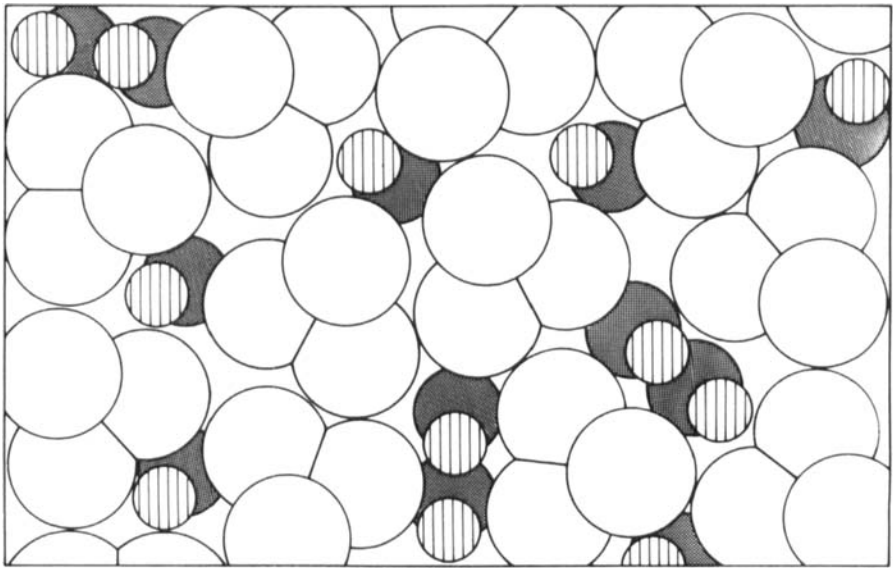


FIGURE 4

Silica surface for maximum TMS-coverage; Si-O-Si bond angle of 150°
significance of circles as in fig 3; enclosed area in fig.3 and 4 equal to 4.6 nm²

hydroxyls and 0.6 pairs of bound hydroxyls. Consequently, within a rectangular area of 4.60 nm^2 presented in figs. 3 and 4 we must fit 10.6 TMS groups, 6 free hydroxyl groups and 2.8 pairs of bound hydroxyl groups.

Figure 3 illustrates that for a Si-O-Si bond angle of 110° no screening of unreacted hydroxyl groups is required to fit all molecules. For a bond angle of 150° figure 4 shows that partial screening of unreacted hydroxyl groups is absolutely necessary. In fact, it takes patience to move the molecules around within the frame of 4.6 nm^2 untill a picture as shown in figure 4 is obtained.

For the PDS molecule similar pictures could be made provided we know the tilt of the phenylring. It is readily argued, however, that a Si-O-Si bond angle of 150° would be difficult to realize. Indeed, the minimum cross-section of a PDS-molecule is stated in column D of Table 4 to be 0.39 nm^2 for this bond angle. Hence, with a maximum coverage of 2.1 PDS molecules per nm^2 this would take up 0.82 nm^2. This is significantly larger than the area of 0.75 nm^2 occupied by 2.3 TMS molecules. Consequently, we have not been able to construct a picture similar to figure 4 for the PDS molecule. There is simply not enough free space left for the unreacted hydroxyl groups. For this reason we consider a Si-O-Si bond angle of 150° unrealistic. A maximum value of 140° is more probable.

From figures 3 and 4 it is possible to derive the percentual areas covered by TMS and by unreacted free hydroxyl groups, respectively and the percentage of the surface that is left free, i.e. not covered by any molecule. For the PDS-phase similar data can be calculated for Si-O-Si bond angles up to 120°, since all hydroxyls are completely unscreened then. The data are presented in Table 5.

It is seen that the free surface area at the silica surfaces decreases gradually with increasing Si-O-Si bond angle. For PDS this decrease is more pronounced than for TMS. It is further noted, that for bond angles between 110 and 120° the free surface areas are nearly the same for the TMS and the PDS-phase. Actually, however, a bond angle of 110° is ruled out by the size of the CH_3-group as shown in fig. 2a. Consequently, a minimum Si-O-Si bond angle of 120° is more realistic and quite plausible on the basis of the data presented in Table 5. Together with the upper limit of 140° estimated above, we conclude that the Si-O-Si bond angle of chemically bonded phases is between 120 and 140°. This conclusion agrees very well with the range of 130 to 140° reported by Noll [35].

From a chromatographic point of view, the data presented in Table 5 demonstrate greater coverages than 2.3 TMS and 2.1 PDS molecules per nm^2 cannot be expected. Even more important is the conclusion to be drawn from figures 3 and 4 that the unreacted hydroxyl groups are virtually inaccessible to all but extremely small molecules. Consequently, the chromatographic activity of unmodified hydroxyl groups to solute molecules separated on chemically bonded phases is reduced to long-range interactions extending over the length of the bonded silane molecule. Obviously, the influence of such long-range effects diminishes rapidly with increased chain length of the organosilane molecule. Therefore we can fully agree with Karch and Halász [42] that after a chain-length of about four carbon atoms the influence of remaining hydroxyl groups is negligible provided that maximum coverage has been reached. Naturally, this need not be true if the silica surface is only partially modified by silane molecules.

For small silane molecules, such as TMS and PDS long-range activity of remaining hydroxyl groups cannot be ruled out a priori. Such effects would be more pronounced for smaller Si-O-Si bond angles (120°) than for larger Si-O-Si bond angles (140°), since in the latter situation the hydroxyl groups are partially screened. In this respect chromatographic experiments regarding the relative polarity of the TMS-phase and the PDS-phase should be helpful. For example, if both phases display the same polarity, then the polarity is probably due to long-range effects of free hydroxyls ma-

TABLE 5

PERCENTUAL COVERAGE OF THE SILICA SURFACE

Si-O-Si angle	TMS-PHASE			PDS-PHASE		
	TMS groups	non or partly screened OH groups	unoccupied surface area	PDS*) groups	non or partly screened OH groups	unoccupied surface area
150°	75	13	12	82	~ 9**)	~ 9**)
120°	66	17	17	68	17	15
110°	65	17	18	63	17	20

*) the minimum values of column D in Table 4 are used

**) estimated values

king a Si-O-Si bond angle of 120° more probable. If, on the other hand, the TMS-phase is found to be more polar then the PDS-phase this is still due to free hydroxyls, but the Si-O-Si bond angle should be close to 140° to explain the more extensive screening by the larger PDS molecules. Finally, if the PDS-phase is observed to be more polar than the TMS-phase, free hydroxyls are probably unimportant and the observed difference is attributed to the different polarity between the phenyl group and the methyl group. In this situation the Si-O-Si bond angle could take any value between 120 and 140°. Actually, of course, the Si-O-Si bond angle will not be fixed at a particular value equal for all silane molecules. The picture that emerges from figures 3 and 4 and from Table 5 can be visualized as follows. The first silane molecules that react with the silica surface can choose the hydroxyl groups freely and assume any position they like. As more and more silane molecules react with the silica surface they will find it increasingly more difficult to find accessible hydroxyl groups. The last silane molecules to react with the surface must actually squeeze in between the silane molecules already present and in doing so will force these molecules to adapt their positions and bond angles to suitable values within the range stated. When the reaction ends and maximum coverage has been obtained, there is very little unoccupied area left on the silica surface. The silane molecules are in a rigid position where they cover some 70% of the silica surface. Remaining hydroxyl groups are only partly screened and cover an additional 15% of the silica surface. About 15% of the surface remains unoccupied by any molecule.

CONCLUSIONS

The results derived from the geometrical model developed for chemically bonded TMS and PDS phases can be summarized as follows.

1. If the structure of amorphous silica resembles that of crystalline silica distorted due to ruptured Si-O bonds, then the total surface density of 4.8 hydroxyl groups per nm^2 can be separated into 0.6 pairs of bonded hydroxyl groups per nm^2 and 3.6 free hydroxyl groups per nm^2.

2. The free hydroxyl groups are more reactive towards chlorosilanes than the bonded hydroxyl groups.

3. For both the TMS and the PDS phase the maximum coverage corresponds to 70% of the silica surface. Half of the remaining area is taken up by unmodified hydroxyl groups, so that only 15% of the silica surface remains completely unoccupied. This efficient coverage of the surface makes it improbable that greater densities than 2.3 TMS or 2.1 PDS per nm^2 can be realized.

4. In the case of maximum coverage the TMS and PDS molecules are rigidly attached to the silica surface with a Si-O-Si bond angle between 120 and 140 degrees. Geometric and energetic considerations make free rotation either impossible or unfavourable.

5. Unreacted hydroxyl groups are quite inaccessible when maximum coverage has been reached. Chromatographic retention due to remaining hydroxyl groups can only be expected from long-range interactions extending over the length of the bonded silane molecule.

6. In the PDS-phase the phenyl group points away from the silica surface. A fortiori the same result is predicted for long-chain organosilanes.

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