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GEOMETRIC STRUCTURAL PROPERTIES OF BONDED LAYERS OF CHEMICALLY MODIFIED SILICAS

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SUMMARY

The effects of the support structure and the modifier structure on the characteristics of chemically modified stationary phases (bonding density, thickness of the bonded layer) were studied and the principle of geometric structural conformity was formulated. It has been demonstrated that reversed phases can be divided into "rigid", "flexible" and intermediate structures of a bonded layer. Only structurally uniform stationary phases have been found to possess similar properties.

INTRODUCTION

Silicas chemically modified with organic compounds are the main type of stationary phases used in liquid chromatography. Reversed phases containing groups with long hydrocarbon chains bonded to silica are important as stationary phases and more than half of all analyses by high-performance liquid chromatography (HPLC) use reversed phases. A comparison of reversed phases with similar compositions shows that their characteristics may be very different, and this is not easily explained[1,2].

The complexity of these materials can be illustrated with the simplest models of the arrangement of bonded hydrocarbon chains[3]. The number of bonded modifier groups per unit surface area (bonding density) depends on the pore structure of the support. For instance, when the diameter of a pore does not exceed 11 nm, the bonding density of C_{18} stationary phases decreases as the diameter becomes smaller[4]. A decrease in bonding density leads to alterations in the bonded layer thickness and to an increase in the amount of residual unreacted silanol groups of silica. In most instances uncontrolled bonding density and bonded layer thickness are the main reason for the variations in the adsorptive and chromatographic properties of silicas that have similar chemical compositions, *e.g.*, C_{18} stationary phases.

This paper presents an analysis of the effects of the pore structure of support on the characteristics of chemically modified stationary phases (bonding density, thickness of bonded layer). The principle of geometric structural conformity is formulated. It has been demonstrated that reversed phases can be divided into "rigid",

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"flexible" and intermediate structures of the bonded layer. Only structurally uniform stationary phases have been found to possess similar properties.

MODEL OF MODIFIED SURFACE

The adsorptive and chromatographic characteristics of silicas modified with organic compounds depend to a great extent on the bonding density of the modifier and the bonded layer thickness. The bonding density, p, is the number of modifier molecules per unit surface area, usually per 1 nm^2, and it reaches its maximum value, p_{max}, on flat or permanent surfaces and depends on the dimensions of the modifier. The maximum value of the bonding density is determined by the minimum permitted distance between points of fixation of the modifier molecules, L_{min}. A decrease in bonding density causes an increase in the number of unreacted silanol groups, which can change the adsorptive and chromatographic characteristics of modified silicas.

In most instances organosilicon compounds are employed as surface modifiers and therfore the sizes of "anchor groups" responsible for fixing modifier molecules on the silica surface [*e.g.*, $-Si(CH_3)_2Cl$ or $-SiCl_3$] determine the minimum distance between two points of fixation on a flat surface, which depends to a minor extent on the residue of the modifier molecule[3,4]. In practice, the value of p can be calculated from carbon analysis data and the specific surface area of silica[5]. On the other hand, the surface concentration of bonded molecules can be expressed by another parameter, L, the mean distance between two points of fixation of bonded molecules. The relationship between these two parameters is[3]

$$p = 1.15/L^2 \tag{1}$$

or

$$L = 1.075/p^{0.5}$$

If $p = p_{max}$, $L = L_{min}$. For alkylsilanes[3,5] $p_{max} = 2.3$ groups per nm^2 and $L_{min} = 0.75$ nm.

The bonded layer thickness, h, is the mean distance between the fixation point of the bonded molecule and its top. The bonded layer thickness is directly connected with the conformation of bonded chains. Straight bonded molecules may extend perpendicular to the support surface to form the so-called "brush" structure of the bonded layer (Fig. 1). Conformational changes of bonded hydrocarbon chains may lead to the formation of the so-called "liquid-like" structure of the bonded layer (Fig. 1). When proceeding from one extreme case to the other the bonded layer thickness

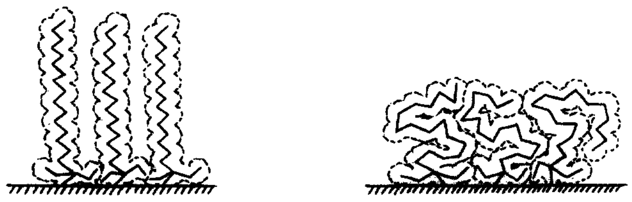

Fig. 1. "Brush" and "liquid-like" structures of bonded layer of silica modified with n-alkylsilanes.

almost doubles. The differences in bonded layer thickness may lead to distinctions in the retention mechanism of a sample on chemically modified stationary phases. Hence the bonded layer thickness is an important parameter of bonded phases.

On passing from a flat to a concave surface the bonding density does not depend on the anchor group size but is determined by steric hindrance that occurs when the upper parts of the bonded molecules come into contact (Fig. 2). The experimental data show[4] that the bonding density is lower in small pores, which means that the mean distance between fixation points of bonded molecules is longer than that obtained with a surface that is close to flat. These changes affect the conformational transitions of bonded molecules and therefore the thickness of the bonded layer also alters.

To calculate p and h for chemically modified porous silica stationary phases we choose the following model: the support contains cylindrical pores (this is the most generally accepted view of the porous silica structure); the mean distance between fixation points of bonded molecules in pores of equal diameter is constant; and bonded hydrocarbon chains have a conformation that provides the maximum bonding density, as follows from the irreversibility of the reaction of organosilicon compounds with a silica surface carried out with an excess of a modifier during the time required to complete the reaction.

Within the framework of the suggested model, it is easy to evaluate the pore diameter D^* at which steric hindrance of attached chains will appear. Indeed, for a bonded molecule of length l a similarity correlation will give

$$\frac{L_{\min}}{d} = \frac{D^*}{D^* - 2l}$$

Hence

$$D^* = \frac{2l}{L_{\min} - d} \tag{2}$$

where $L_{\min}$ is the minimum distance between two anchor groups on a flat surface, d is twice the Van der Waals radius of a methyl group and l is the length of the molecule

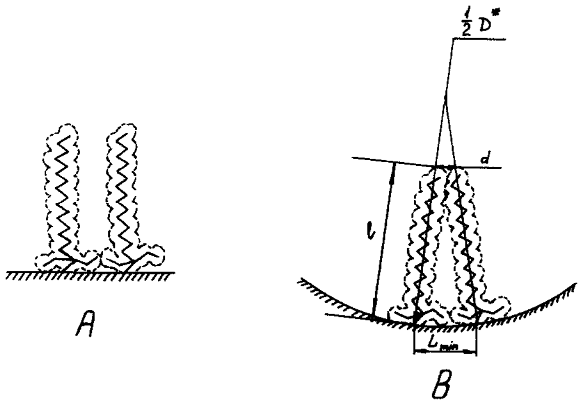

Fig. 2. Steric hindrance arising on passing from (A) a flat to (B) a concave surface of a cylindrical pore of diameter D^*.

TABLE I

VALUE OF D^* FOR DIFFERENT BONDED MODIFIER MOLECULES

Modifier	D^* *(nm)*
$-C_8H_{17}$	4.9
$-C_{16}H_{33}$	9.8
$-C_{18}H_{37}$	10.8
$-(CH_2)_{10}CN$	6.1

as the sum of the bond lengths, and taking into account the angles between them (Fig. 2). For example, for octadecyldimethylchlorosilane[3] l = 2.45 nm, L_{min} = 0.75 nm, d = 0.4 nm and D^* will be 10.8 nm. This means that if the pore diameter is less than D^* the bonded molecules are exposed to mutual steric hindrance. The data calculated from eqn. 2 for different bonded molecules are given in Table I.

Let us consider in detail the state of bonded hydrocarbon chains in small pores (pores with diameter D less than D^*). In conformity with the principle of maximum bonding density, long-chain *n*-alkyl chains have a conformation that provides the most compact packing of bonded molecules on a surface, as is possible, for instance, when the *n*-alkyl chains are "folded" (Fig. 3).

Further, we consider the bonded *n*-alkyl chain as a cylinder standing perpendicular to the surface, its height and diameter being h and q, respectively. Then the conformational transitions of bonded chains will be determined as changes in h and q. It should be noted that the height of the cylinder is the thickness of the bonded layer. There is an evident connection between h and q; thus, considering the molecule volume constant, $V_{mol} = \pi h q^2/4$, we have

$$q = \sqrt{\frac{4V}{h\pi}}$$

Then geometric consideration of the pore diameter D ($D < D^*$) gives (Fig. 3)

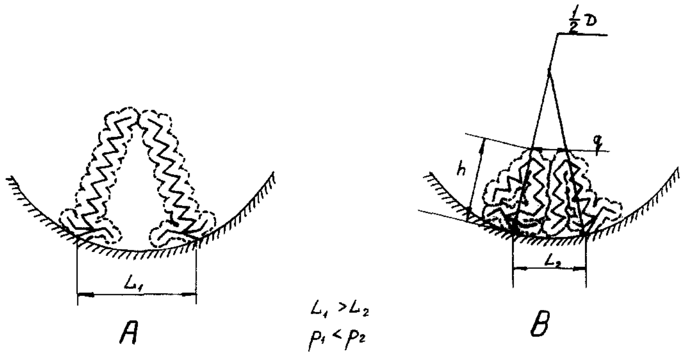

Fig. 3. Model of collision of bonded chains. (A) Alkyl chains as straight as possible; (B) alkyl chains with a conformation providing a denser attachment.

$$L = \frac{Dq}{D-2h} \tag{3}$$

and therefore the bonding density, assuming $q = \sqrt{4V/h\pi}$, is expressed by

$$p = \frac{1.15}{L^2} = \frac{1.15h(D-2h)^2\pi}{4VD^2} \tag{4}$$

The analysis of the first derivative of $p(h)$ shows that it has the only extreme value (for h from 0 to $D/2$) at $h = D/6$ (Fig. 4) and the value of the bonding density at $h = D/6$ is

$$p\left(h = \frac{D}{6}\right) = \frac{1.15D\pi}{54V} \tag{5}$$

Therefore, for a pore diameter D, the greatest bonding density is obtained when the conformation of the bonded molecules provides a bonded layer thickness equal to $D/6$. For silicas with bonded octadecyl groups with pore diameters less than 10.8 nm we have

$$p = 0.217D \tag{6}$$

$$h = \frac{D}{6} \tag{7}$$

The p and h data calculated from eqns. 6 and 7 for C_{18} bonded phases are given in Table II.

Hence within the framework of the suggested model the bonding density decreases linearly with decrease in pore diameter when D is less than D^*. If the pore diameter is 6 nm, the bonding density reaches only 55% of the maximum possible value, p_{max}, obtained on a flat surface or in pores with D greater than D^* (Table II). A decrease in the bonding density causes an increase in the number of unmodified silanol groups and, hence, changes in the adsorption characteristics of stationary phases. As the diameter decreases, bonded molecules must fold more densely to pro-

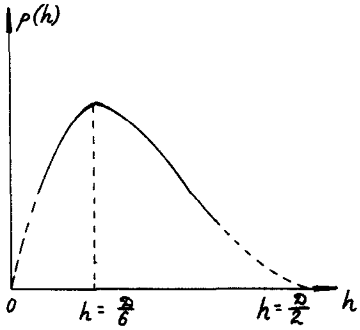

Fig. 4. Dependence of bonding density on conformation of alkyl chains (bonded layer thickness).

TABLE II

BONDING DENSITIES AND BONDED LAYER THICKNESSES OF OCTADECYLDIMETHYLSILYL STATIONARY PHASES WITHIN PORES OF DIFFERENT DIAMETER CALCULATED USING EQNS. 6 AND 7

Parameter	*Pore diameter (nm)*			
	10.8	*10.0*	*8.0*	*6.0*
Bonding density (groups per nm^2)	2.30	2.17	1.70	1.30
Bonded layer thickness (nm)	1.85	1.66	1.50	1.00

vide a more compact packing, in other words, to ensure the maximum bonding density for a given pore. Simultaneously, the bonded layer thickness also decreases linearily with decreasing pore diameter.

We should point out that the maximum bonding density (in pores with $D < D^*$) can be achieved through a strictly specific thickness. This also means that the bonded layer is thickened and the mobility of bonded chains is limited. This state of a bonded layer has been termed a "rigid" structure (Fig. 3b).

In contrast to stationary phases with rigid structure, the so-called "flexible" structure is realised in wide pores (with $D > D^*$). In this instance bonded molecules are not exposed to mutual steric hindrances and, depending on the external conditions, they may change their conformation over a wide range (Fig. 1).

CALCULATION AND EXPERIMENTAL DETERMINATION OF BONDING DENSITY

So far we have not taken into account the pore size distribution. To compare the results predicted by theory with experimental data and to study real stationary phases, the distribution of pore size should be taken into account.

The bonding density at $D > D^*$ corresponds to the highest possible value; for example, for trichloro-and dimethylalkylchlorosilanes it is 2.3 groups per nm^2. The bonding density for $D < D^*$ may be calculated from eqn. 4. Thus, taking into consideration the pore size distribution for the bonding density, we obtain the following relationship:

$$p = \int_{D_1}^{D^*} p(D) \frac{1}{\sigma\sqrt{2\pi}} \exp\left[- \frac{(D-D_0)^2}{2\sigma^2} \right] \mathrm{d}D \left(\frac{S_1}{S_1+S_2} \right) + p_{\max} \left(\frac{S_2}{S_1+S_2} \right) \quad (8)$$

It is accepted here that pore size distribution obeys a normal law with parameters D_0 and σ. Integrating eqn. 8 with respect to diameter from the smallest diameter D_1 to D^* we obtain the bonding density p for $D < D^*$. The bonding density for $D > D^*$ is $p_{\max}$. S_1 and S_2 are the specific surface areas corresponding to definite intervals of diameter, *viz.*, S_1 from D_1 to D^* and S_2 from D^* to the largest diameter D_2.

Using eqn. 8 we calculated the bonding densities for a number of chemically modified silicas with different pore structures (D_0, σ) and kinds of modifier. The calculated data are given in Table III. It can be seen that the calculation agrees well with the experimental data. Unfortunately we are not in a position to treat the data in all the publications concerning the reaction of chemical modification of silica, because in order to perform calculations in conformity with eqn. 8 one needs, in addition to D_0, the value of σ, *i.e.*, the shape of pore size distribution curve must be known.

Let us consider the determination of S_1, S_2, D_0 and σ from the experimental $\mathrm{d}V/\mathrm{d}D$ curve. One can construct the curve of pore size distribution as a function of diameter from the desorption part of the sorption isotherms[6]. For calculation with eqn. 8, for instance, it is necessary to pass to a distribution $\mathrm{d}N/\mathrm{d}D$, where N is the number of pores of a fixed diameter. To pass from $\mathrm{d}V/\mathrm{d}D$ to $\mathrm{d}N/\mathrm{d}D$, one can use the following relationship:

$$\frac{1}{V_0} \cdot \frac{\mathrm{d}V}{\mathrm{d}D} = \frac{\pi D^2 f}{4} \cdot \frac{\mathrm{d}N}{\mathrm{d}D} \cdot \frac{1}{N_0} \tag{9}$$

assuming that the pores are cylinders of depth f. With a normal distribution $\mathrm{d}N/\mathrm{d}D$ the connection between the distribution parameters is evident. Indeed,

$$\left[\frac{\mathrm{d}}{\mathrm{d}D}\left(\frac{\mathrm{d}V}{\mathrm{d}D}\right)\right]_{D=D_\mathrm{m}} = \frac{\mathrm{d}}{\mathrm{d}D}\left\{\frac{\pi D^2 f}{4} \cdot \frac{1}{\sigma\sqrt{2\pi}} \cdot \exp\left[-\frac{(D-D_0)^2}{2\sigma^2}\right]\right\} = 0 \tag{10}$$

from which

$$D_0 = D_\mathrm{m} - \frac{2\sigma^2}{D_\mathrm{m}} \tag{11}$$

where D_m is coordinate of the maximum of the distribution $\mathrm{d}V/\mathrm{d}D$.

TABLE III

BONDING DENSITIES OF HEXADECYLDIMETHYLCHLOROSILANE (C_{16}) AND CYANODECYLTRICHLOROSILANE ($C_{10}CN$) FOR SILICAS OF DIFFERENT PORE STRUCTURE CALCULATED USING EQN. 8 AND EXPERIMENTAL DATA

Modifier	*Characteristics of pore structure of original silicas*				*Bonding density (nm^{-2})*	
	D_0 (nm)	*σ (nm)*	$\frac{S_1}{S_1+S_2}$	$\frac{S_2}{S_1+S_2}$	*Calculated*	*Experimental*
C_{16}	25	3	0	1	2.3	2.1 ± 0.15
C_{16}	13.0	3	0.66	0.34	1.9	2.0 ± 0.15
C_{16}	11.5	1.5	0.35	0.65	1.9	1.9 ± 0.15
C_{16}	5.3	1.0	1	0	1.3	1.4 ± 0.15
$C_{10}CN$	6.8	1.5	0.5	0.5	1.5	1.6 ± 0.15

A second ratio is obtained on equating to zero the second derivative of $\mathrm{d}V/\mathrm{d}D$ at the inflection point $D = D_i$:

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}D^2}\left(\frac{\mathrm{d}V}{\mathrm{d}D}\right)\right]_{D=D_i} = \frac{\mathrm{d}^2}{\mathrm{d}D^2}\left\{\frac{\pi D^2 f}{4}\cdot\frac{1}{\sigma\sqrt{2\pi}}\cdot\exp\left[-\frac{(D-D_0)^2}{2\sigma^2}\right]\right\} = 0 \tag{12}$$

hence we obtain

$$\sigma^4 - 0.5\sigma^2\left[4D_i(D_i-D_0)+D_i^2\right] + 0.5D_i^2(D_i-D_0)^2 = 0 \tag{13}$$

From the values of D_i and D_m we can find D_0 and σ. We analysed a large number of $\mathrm{d}V/\mathrm{d}D$ distributions and established that σ can be calculated as $\frac{1}{3}(D_m - D_1)$, where D_1 is the smallest value of the pore diameter. If σ is negligible compared with D_m then $D_0 = D_m$ (see eqn. 11). With a wide and/or asymmetric distribution of $\mathrm{d}V/\mathrm{d}D$, D_0 can differ significantly from D_m and should be calculated from eqn. 11.

S_1 and S_2 were calculated using the equation $S = 4V/D$. Hence

$$S_1 = \int_{D_1}^{D^*}\frac{4V}{D}\cdot N(D_0;\ \sigma)\mathrm{d}D \tag{14}$$

$$S_2 = \int_{D^*}^{D_2}\frac{4V}{D}\cdot N(D_0;\ \sigma)\mathrm{d}D \tag{15}$$

where V is the pore volume (ml/g) and $N(D_0;\ \sigma)$ is the normal distribution with parameters D_0 and σ:

$$N(D_0;\ \sigma) = \frac{1}{\sigma\sqrt{2\pi}}\cdot\exp\left[-\frac{(D-D_0)^2}{2\sigma^2}\right]$$

DETERMINATION OF BONDED LAYER THICKNESS

The bonded layer thickness is experimentally determined from the change in a pore volume after chemical modification. Assuming that the pores have a cylindrical form, one can obtain the relative change in pore volume as follows:

$$\frac{\Delta V}{V} = \frac{4f\pi[D^2-(D-2h)^2]}{4f\pi D^2} = 1 - \frac{(D-2h)^2}{D^2} \tag{16}$$

where D is the average pore diameter and h is the average bonded layer thickness. Solving this equation for h we obtain

$$h = D\left(0.5 - \sqrt{1 - \frac{\Delta V}{4V}}\right) \tag{17}$$

i.e., if we know the change in pore volume ΔV we can determine the average bonded layer thickness.

It is wrongly thought that the bonded layer thickness is equal to half the difference in the average pore diameters obtained from the pore volume distribution before and after modification:

$$h = 0.5(D_m - D_m^M) \tag{18}$$

Average diameters are determined from desorption curves, reconstructed into differential curves of pore volume distribution *versus* diameter. However, as was mentioned before, the average pore volume distribution is not equal to the average distribution of the number of pores, namely,

$$D_0 = D_m - \frac{2\sigma^2}{D_m}$$

Hence it is correct to write

$$h = 0.5(D_0 - D_0^M) \tag{19}$$

This equation, unfortunately, is not taken into account by many workers, which has led to discrepancies in data on bonded layer thickness and erroneous conclusions about the conformational structures of bonded molecules. For example, in one study[7] the conclusion about the "brush" structure of a bonded layer was made on the basis of the coincidence of values of the length of a molecule understood as the sum of bond lengths and h as $0.5(D_m - D_m^M)$, whereas calculation on the basis of eqn. 17 gives far smaller values for the thickness, which demonstrates a liquid-like structure as preferred. In Table IV the values of bonded layer thickness for hexadecyl- and octadecylsilyl stationary phases calculated using eqns. 17 and 18 are given, and it can be seen that they are different. With a wide and asymmetric distribution the dispersion of h values can be especially significant. Indeed, $0.5(D_m - D_m^M) = 0.5(D_0 - D_0^M)$ if σ is negligible.

Let us consider a typical example. Sample 4 (Table IV) has an asymmetric pore size distribution with a large tail in the range of small pores. This fact is likely to account for a smaller value of the bonded layer thickness than for sample 2. In fact, the bonded layer thickness in small pores is less than in large pores, but the surface area of these pores is considerable. The average value of the bonded layer thickness is reduced although one would think that a sample with $D_0 = 13$ nm should at least have a bonded layer thickness equivalent to that of sample 2 with $D_0 = 11.5$ nm (Table IV). The modified silicas studied by Roumeliotis and Unger[7] are likely to have had analogous asymmetric pore size distributions, which resulted in the excessive h values obtained using eqn. 18.

The average bonded layer thickness can be also determined from the change in the specific surface area after chemical modification:

$$\frac{\Delta S}{S} = \frac{f[\pi D - \pi(D-2h)]}{fD\pi} = \frac{2h}{D} \tag{20}$$

However, the precision of measurement of S for modified silicas is low, because the value of the adsorption ground (*i.e.*, the average area per molecule within the BET monolayer) of an adsorbate molecule in the bonded layer is unknown.

In our opinion, the most precise and simplest approach to the determination of bonded layer thickness is to apply eqn. 17 using experimental data obtained from the change in pore volume after chemical modification. When using eqn. 17 one should replace V^{M} with a value that takes into account the excess weight of sorbent as a result of modification:

$$V^{M}_{corr} = \frac{V^{M}}{100-M} \tag{21}$$

where M (%) is the excess weight due to the modifier.

Analysis of the values of bonded layer thickness given in Table IV demonstrates that, first, the bonded layer thickness, as was predicted by theory, falls as the average pore diameter decreases starting from a certain value (approximately 10 nm for C_{16} stationary phases). Second, as follows from the h value, the bonded layer does not have a "brush" structure but closer to a liquid-like structure.

The absorption methods can give values close to the actual values only for stationary phases with a rigid structure of the bonded layer, *i.e.*, when the conformational transitions of bonded alkyl chains and the penetration of absorbable molecules, for instance benzene, into the bonded layer are hindered.

CALCULATION OF BONDED LAYER THICKNESS

We have found that for the pores with a diameter D less than D^* the optimum

TABLE IV

BONDED LAYER THICKNESSES OF SILICAS MODIFIED WITH HEXADECYL-(C_{16}) AND OCTADECYLDIMETHYLCHLOROSILANE (C_{18}) CALCULATED USING EQNS. 17 AND 18

Modifier	*D_0 (nm)*	*Bonded layer thickness (nm)*	
		From eqn. 17	*From eqn. 18*
C_{16}	25.0	1.2	0
C_{16}	11.5	1.1	1.4
C_{16}	5.3	0.85	0.5
C_{16}	13.0	0.95	2.0
C_{16}	13.4	0.94	2.2*
C_{18}	10.0	1.1	1.5**

* According to ref. 7.
** According to ref. 8.

bonded layer thickness is a strictly definite value which provides the densest attachment:

$$h = \frac{D}{6}$$

For a pore size distribution including values up to D^* the thickness of the bonded layer can be calculated by integrating eqn. 22 with respect to diameter. Unfortunately, within the framework of the suggested model we cannot evaluate the bonded layer thickness at values of D larger than D^*, *i.e.*, in wide pores. The answer to this problem can only be obtained by a direct experiment, for instance, by Fourier transform (FT) IR spectroscopy for wide-pore modified silicas. As has been shown[9]. the application of this method permits the evaluation of the number of gauche defects for a bonded alkyl chain and thus gives direct information about the conformation of bonded molecules. Only in this case for the bonded layer thickness can an equation analogous to eqn. 8 be obtained, namely

$$h = h_1 \cdot \frac{S_1}{S_1+S_2} + h_2 \cdot \frac{S_2}{S_1+S_2} \tag{22}$$

Within the framework of the available model we can only calculate h_1 equal to $D/6$. It is interesting that values depending on the kind of molecule (for instance, the number of methylene links) are not included in equation for h_1. However, the contribution of the first term for bonded hydrocarbons of different lengths will vary as the value of D^* depends on the length of the modifier molecules.

A comparison of the h values, calculated using eqn. 22 with the bonded layer thicknesses, calculated using eqn. 17 on the basis of experimental data obtained from the change in pore volume as a result of chemical modification for pores with D less then D^* is presented in Table V.

CONCLUSIONS

The geometric structural consideration of the bonded layer of chemically modified silicas has shown that modified silicas have very complicated structures. The

TABLE V

BONDED LAYER THICKNESSES, CALCULATED USING EQN. 21, AND EXPERIMENTAL DATA FOR SILICAS MODIFIED WITH HEXADECYLDIMETHYLCHLOROSILANE (C_{16}) AND OCTADECYLDIMETHYLCHLOROSILANE (C_{18})

Modifier	*D_0 (nm)*	*Bonded layer thickness (nm)*	
		Calculated	*Experimental*
C_{18}	6.6	1.10	1.03*
C_{16}	5.3	0.88	0.86

* Data calculated using eqn. 17 on the basis of experimental results from ref. 7.

principal characteristics of the bonding density and thickness of the bonded layer depend on a number of parameters, *viz.*, pore structure of the support, kind of modifier and conditions of modification. Even very small changes in one of these parameters, *e.g.*, the average pore diameter, from batch to batch may cause uncontrollable changes in the state of the bonded layer and, hence, the chromatographic properties.

On the basis of this study, surface conformational structures can be divided into three groups, rigid, flexible and intermediate (mixed).

In the rigid structure the diameter of the support pores does not exceed the collision diameter D^*. The bonded molecules are exposed to steric hindrance. Conformational transformations are hampered or impossible. The bonded layer thickness is unchangeable and is equal to $h = D/6$. The bonding density is less than the maximum value, p_{max}, and the bonded layer thickness decreases linearly as the pore diameter diminishes. This layer is characterized by an adsorptive retention mechanism as the sample molecules can hardly penetrate the bonded layer.

In the flexible structure the diameter of the support pores is larger than the collision diameter D^*. The bonded molecules are virtually on a flat surface. Conformational transformations are permitted and the sample molecules can penetrate the bonded layer. The bonding density is equal to the maximum value, p_{max}, and is constant throughout the surface. The bonded layer thickness depends on the solvent and temperature.

In the intermediate (mixed) structure, if the average pore diameter is equal to the collision diameter, but if D for a number of pores is less then $D_0 = D^*$, these pores contain the rigid structure of the bonded layer and the remainder of the pores contain the flexible structure. In this instance the retention mechanism is intermediate.

Stationary phases that possess an intermediate structure are the most complicated. Indeed, even trivial alterations in the average pore diameter can substantially change the ratio of rigid structure to flexible structure, which can affect the chromatographic properties of the stationary phase.

For instance, for C_{18} stationary phases $D^* = 10.8$ nm. If a support does not contain pores with the diameter up to 10.8 nm (this is especially true of supports with an average pore diameter of 4–8 nm) the structure of the bonded layer is rigid. If the average pore diameter is close to 10.8 nm (namely 8–14 nm) the intermediate structure is realised. It should be noted that most commercial stationary phases are obtained on the basis of such supports, and therefore they differ considerably in their chromatographic properties.

When the average diameter is greater than or equal to 14 nm, the bonded layer has the flexible structure. In our opinion, these stationary phases are probably the most reproducible, as their attachment density does not depend on the pore diameter. Hence, even marked differences in the pore diameter of different batches of support can affect the capacity factor but not their selectivity.

Consideration of the geometric structural features of the bonded layer structure within the framework of the model of cylindrical pores demonstrates a good coincidence with experimental data for the average bonding density and average bonded layer thickness. However, one should not forget that in reality stationary phases are much more complicated than theoretical models. A considerable proportion of stationary phases have a globular structure, *i.e.*, they are formed in gaps

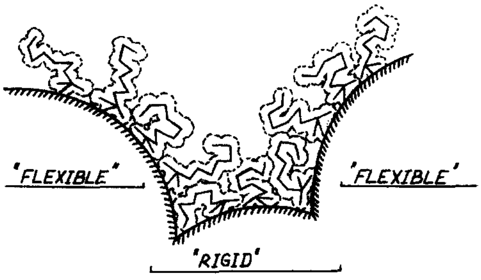

Fig. 5. Flexible and rigid structures within pores formed by primary particles of silica.

between primary globes. This structure of the pore surface should result in the formation of a rigid structure of the bonded layer in the areas close to the contact points of globes and a flexible structure on the tops of the globes. Thus, even pores of equal diameter have various bonding densities and structures of the bonded layer in different areas of the surface. The modified surface in such pores has a mozaic-like structure, each pore having sections of flexible and sections of rigid structure. An increase in the pore diameter leads to an increase in the proportion of the flexible structure and a decrease in the pore diameter leads to an increase in the proportion of the rigid structure (Fig. 5).

Geometric analysis shows that the distribution of the types of bonded layer structure in globular pores differs only insignificantly from that in cylindrical pores. For instance, C_{18} stationary phases with a pore diameter less than 7 nm actually do not contain the flexible structure at all, whereas stationary phases with a pore diameter of more than 14 nm mainly contain the flexible structure.

In recent years many papers have been devoted to the study of the bonded layer structure of reversed phases by different methods such as FT-IR spectroscopy[9], NMR spectroscopy[10,11] and luminescense spectroscopy[12].

In our opinion, when interpreting experimental data and deducing general regularities, one should have an idea of the complexity of the object being studied. Therefore, it is hardly reasonable to choose a sample with an intermediate structure as the model for studying the physico-chemical properties of the bonded layer. In our opinion, one can compare only structurally equivalent stationary phases with flexible or rigid types of structure prevailing. We mean here the analysis of the bonded layer characteristics such as the adsorptive capacity and selectivity of the bonded layer and the mobility of bonded molecules. This is the expression of the geometric structural correspondence principal.

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