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EFFECT OF ALKYL CHAIN LENGTH ON SURFACE SILANIZATION OF SILICA

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SUMMARY

The effect of the chain length of *n*-alkyldimethylchlorosilane on surface silanization was extensively studied. The alkyl surface concentrations for primary and endcapping silanization were determined using a more accurate gravimetric method instead of the conventional carbon analysis, and the residual hydroxyl groups were detected by a modified Sears' titration method. It was found that there was a linear relationship between the alkyl surface concentration and the number of carbon atoms in the chain of the silane for the primary bonding. It was also found that the total alkyl surface concentration after endcapping remained the same irrespective of the different silanes employed in the primary bonding. It was confirmed that the sum of total alkyl concentration and residual hydroxyl surface concentration equaled the original hydroxyl surface concentration for low-temperature silanization. Compared with previous data, the present study revealed that micropores would considerably decrease the alkyl concentration for long-chain silanes. A size-exclusion mechanism is proposed, tentatively, to interpret the chain-length effect on silanization.

INTRODUCTION

Reversed-phase materials are now the most popular packing materials in high-performance liquid chromatography (HPLC) and are widely used in routine analysis. Commercial silica-based packings are available with methyl-, *n*-propyl-, *n*-octyl- and octadecyl-bonded functional groups. Since trichloro- and dichlorosilanizing reagents can result in high surface concentrations of hydroxyl groups due to hydrolysis of Si–Cl groups[1], *n*-alkyldimethylmonochlorosilane is usually utilized to modify the silica surface.

The alkyl chain length and the alkyl surface concentration are two critical parameters which determine the hydrophobicity of a packing material, and thus determine retention and selectivity characteristics[2].

Some aspects of the influence of *n*-alkyl chain length on alkyl surface concentration have been reported by several investigators[1,3].

In this study the effect of the chain length of *n*-alkyldimethylchlorosilane on

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surface silanization was further studied, and the alkyl surface concentrations for both primary and endcapping silanization were characterized using a more accurate gravimetric method instead of the conventional carbon analysis. The residual hydroxyl groups were determined by a modified Sears' method. This information provides further insight into the effect of chain length on surface silanization of silica. A size-exclusion mechanism is proposed to interpret the chain length effect on the alkyl surface concentration.

CALCULATION

The calculation for the extent of primary silanization was based on the following formulae:

$$W_{so} = W_p - W_c \tag{1}$$

$$W_o = W_{so} - W_s \tag{2}$$

$$C\% = \frac{12 W_o n}{(M - 36.5) W_{so}} \tag{3}$$

$$\Phi = \frac{W_o}{(M - 36.5) W_s} \tag{4}$$

$$\alpha = \Phi / S \tag{5}$$

where

W_p = the weight of the crucible with silica after primary silanization;
W_c = the weight of the tared crucible before filtration;
W_{so} = the weight of modified silica;
W_s = the weight of underivatized silica;
W_o = the weight of organic layer on silica;
C% = the carbon load expressed as weight percent carbon;
M = the molecular weight of silane reagent;
36.5 = the molecular weight of HCl;
n = the number of carbons in one silane molecule;
Φ = the specific alkyl concentration (μmole/g);
α = the alkyl surface concentration (μmole/m^2);
S = the specific surface area of silica (m^2/g).

The calculation for the extent of the endcapping process was based on the following formulae:

$$W'_s = W_s \frac{W'_{so}}{W_{so}} \tag{6}$$

$$W^e_{so} = W_e - W^e_c \tag{7}$$

$$W^e_o = W^e_{so} - W'_{so} \tag{8}$$

$$\mathrm{C_e\%} = \frac{36W_o^e}{72.2W_{so}^e} \tag{9}$$

$$\Phi_e = \frac{W_o^e}{72.2W'_s} \tag{10}$$

$$\alpha_e = \Phi_e/S \tag{11}$$

where

W'_s = the weight of silica which was used for endcapping;
W'_{so} = the weight of the primary silanized silica which is used for the endcapping process;
W_{so}^e = the weight of endcapped silica;
W_e = the weight of the crucible with endcapped silica;
W_c^e = the weight of the tared crucible before filtration;
W_o^e = the weight of organic layer for endcapping only;
$\mathrm{C_e\%}$ = the carbon load (weight percentage) for endcapping only;
72.2 = the molecular weight difference between TMS and HCl;
Φ_e = the alkyl specific concentration for endcapping only;
α_e = the alkyl surface concentration for endcapping only.

The total carbon load, $\mathrm{C_t\%}$, the total alkyl specific concentration, Φ_t, and the total alkyl surface concentration, α_t, were calculated from the following formulae:

$$\mathrm{C_t\%} = \mathrm{C_e\%} + \mathrm{C\%}\frac{W'_{so}}{W_{so}^e} \tag{12}$$

$$\Phi_t = \Phi + \Phi_e \tag{13}$$

$$\alpha_t = \alpha + \alpha_e \tag{14}$$

The calculation of the effectiveness factor (defined as the ratio of the total reacted hydroxyl groups to the total hydroxyl groups present on the surface) is based on the assumption that the bonded alkyl layer and the added *n*-propanol would not affect the quantitative detection of the residual hydroxyl groups in the modified Sears' method.

Consequently, the ratio of the hydroxyl surface concentrations before and after modification would be equal to that of corresponding specific surface areas determined by Sears' method provided that a correction for the weight increase due to modification is made. Hence the effectiveness factor, η, can be calculated from the formula:

$$\eta = 1 - S_e/S \tag{15}$$

where S *and* S_e are the specific surface areas before and after modification, respectively.

If the sum of the alkyl surface concentration and the residual surface concen-

TABLE I

PROPERTIES OF SILANIZED SILICAS

$S = 160\ \mathrm{m}^2/\mathrm{g}$.

Type of modifier	*Designation of product*	*C %*	C_e *%*	C_t *%*	Φ *(μmole/g)*	Φ_e *(μmole/g)*	Φ_t *(μmole/g)*	α *(μmole/m²)*	α_e *(μmole/m²)*	α_t *(μmole/m²)*
n-Octadecyldimethylchlorosilane	ODMS-silica	10.72	0.378	11.071	521.4	123	644.4	3.259	0.769	4.028
n-Octyldimethylchlorosilane	OTMS-silica	6.430	0.171	6.602	592.0	52.2	644.2	3.700	0.326	4.026
n-Propyldimethylchlorosilane	PMS-silica	3.540	0.047	3.584	627.0	14.0	641.0	3.919	0.088	4.007
TMS and HMDS	TMS-silica	2.202	0.000	2.202	640.0	0.0	640.0	4.000	0.000	4.000

tration is equal to the original hydroxyl surface concentration, the hydroxyl surface concentration can be estimated from the formula:

$$\alpha_{OH} = \alpha_t/\eta \tag{16}$$

$$\alpha^e_{OH} = \alpha_{OH} - \alpha_t \tag{17}$$

where α_{OH} and α^e_{OH} are the hydroxyl surface concentrations before and after modification, respectively.

EXPERIMENTAL

The packing materials used were Ultrapack® ODMS (octadimethylsilyl), OTMS (octyldimethylsilyl), PMS (propyldimethylsilyl) and TMS (trimethylsilyl) (Beckman, Berkeley, CA, U.S.A.). The silica used was spherical, from a single lot, with a nominal particle diameter of 10 μm and a pore diameter of 8.5 nm (D_{max}) at the maximum value of pore volume distribution, as well as a narrow range of pore size (5–12 nm; determined by mercury intrusion analysis, Quantachrome).

Small (ca. 3.5 g), accurately weighed (±0.1 mg) amounts of silica were bonded under conditions in which the reaction proceeded maximally to produce each of the packing materials. After the silanization the suspensions of derivatized silica were quantitatively transferred to a tared glass frit crucible (pore size 4–6 μm, capacity 40 ml) (the filtrate was inspected under a 1600 × microscope and was refiltered if any particle was observed), thoroughly washed sequentially with toluene, water, methanol, chloroform and methanol, and dried under vacuum to constant weight.

An accurately weighed portion of each bonded silica was then transferred to a reaction flask and subjected to a second silanization with trimethylchlorosilane. These "endcapped" materials were then washed, dried and weighed as before.

The specific surface area of the original silica was determined by Sears' titration method[4]. The uncovered specific surface area of the endcapped silica was measured by the modified Sears' method in which 50 ml of *n*-propanol were added to disperse the modified silica. The small effect of *n*-propanol on pH was corrected by a blank run, and the uncovered surface area obtained was further corrected for the weight increase resulting from the surface modification.

RESULTS AND DISCUSSION

In this study, the silica was pretreated to achieve a fully hydroxylated silica free of physisorbed water, and the silanization condition with a simple 1:1 stoichiometry was chosen to maximize alkyl surface concentration.

The determination of specific alkyl concentration by the gravimetric method requires very cautious and time-consuming operations; nevertheless it is more sensitive and accurate than conventional carbon analysis because a large amount of sample can be used. The weighing process itself is highly accurate. Additionally, the original carbon content in silica does not interfere with the analysis. The typical variation is estimated to be 0.2% for the specific alkyl concentration. However, the determination of specific surface area by Sears' method is subject to the usual variation.

The percent carbon load, the specific alkyl concentration and the alkyl surface concentration for this experiment are summarized in Table I.

The alkyl surface concentration decreases as the *n*-alkyl chain length increases, and this trend is consistent with the expectation and the relevant literature[1,6].

In practice, the endcapping process is employed to minimize residual hydroxyl groups after the primary silanization in order to improve column performance[5]. Table I shows that endcapping brings about only a small increase in carbon load. There is a maximum value of 0.378% for ODMS-silica and a minimum value of 0.047% for PMS-silica, which cannot be detected by carbon analysis.

It is interestingly found that the total alkyl surface concentration after endcapping remained almost the same for silicas with different primary silanizations. The slightly higher values for ODMS-silica and OTMS-silica were probably due to physical adsorption of the unreacted silanizing reagents in the primary silanization, which could not be completely washed out. The effect of this presence has been often observed in column performance.

The zero value of α_e for TMS-silica indicates the maximum conversion under the present reaction conditions and the excellent reliability of the gravimetric method.

The effectiveness factors and the hydroxyl surface concentrations for these endcapped silicas are listed in Table II. The effectiveness factors for these endcapped silicas are essentially same and have an average value of 0.501, which is in good agreement with the previously reported[6] value of 0.5. The nearly equal effectiveness factor values and the calculated average hydroxyl surface concentration for original silica of 8.02 μmole/m², which is the typical value mentioned in various references, confirm the conservation of the sum of alkyl and residual surface hydroxyl concentrations at low temperatures (*ca.* 110°C), *i.e.* $\alpha_t + \alpha_{OH}^e = \alpha_{OH}$. However, condensation of the hydroxyl groups via siloxane bridges may occur significantly at high temperatures[7]. It is found, surprisingly, that there is a good linear correlation (Fig. 1) between the primary alkyl surface concentration and the number of carbons in the alkyl chain of the modifier (*i.e.* excluding dimethyl groups). This relation can be expressed mathematically by the equation:

$$\alpha = 4.0601 - 0.045n \tag{18}$$

where n is the number of carbons in the alkyl chain of a modifier.

The average molecular cross-sectional area (A_m) of a silyl group can be cal-

TABLE II

EFFECTIVENESS FACTOR AND HYDROXYL SURFACE CONCENTRATION FOR SILANIZATION

Endcapped silica	η *(%)*	α_{OH} *(μmole/m²)*	α_{OH} *(μmole/m²)*
ODMS-silica	50.6	7.96	3.93
OTMS-silica	50.2	8.02	3.99
PMS-silica	50.1	8.00	3.99
TMS-silica	49.5	8.08	4.08
Average	50.1	8.02	4.00

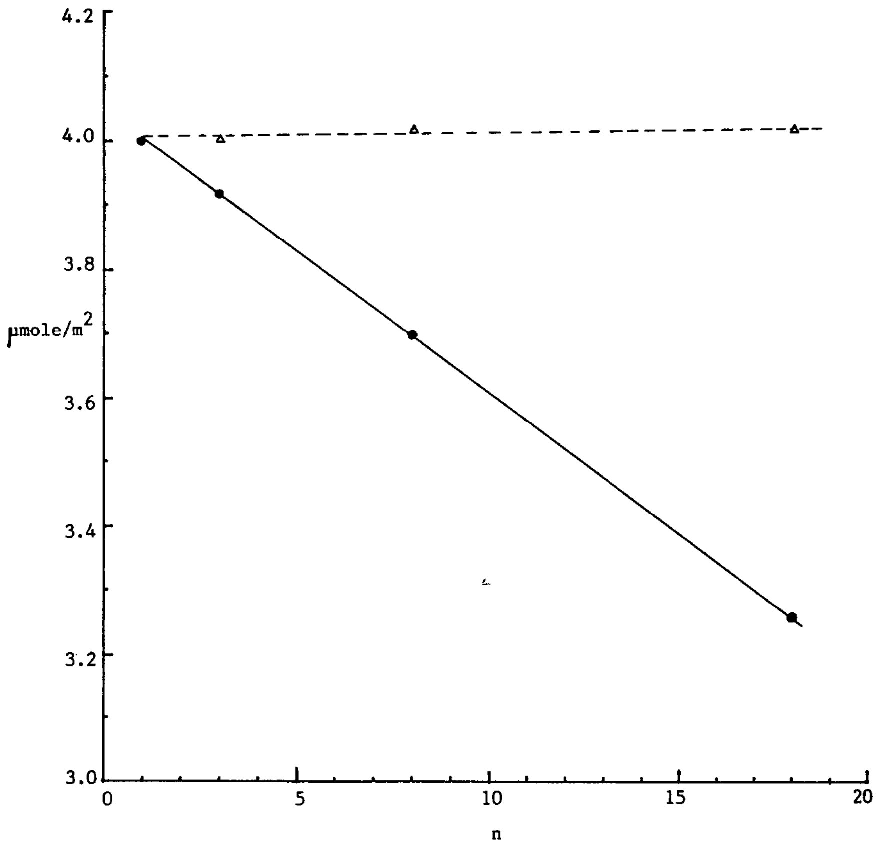

Fig. 1. The primary and total alkyl surface concentration *vs.* the number of carbons in the chain of *n*-alkyldimethylchlorosilane. ●—● = α; △---△ = α_t.

culated from the primary alkyl surface concentration, and in turn the mean distance between two adjacent groups (*B*) can be calculated assuming hexagonal close packing.

Based upon conformational analysis[7,8], *n*-alkyldimethylchlorosilane molecules would have essentially a zigzag arrangement for the skeletal carbon bonds and a tetrahedral structure for each carbon unit. Consequently, the length (*L*) of a molec-

TABLE III

CALCULATED STERIC PARAMETERS

Modifier	A_m (nm^2/molecule)	*B* (nm)	L^* (nm)
ODMS	0.5095	0.7670	2.472
OTMS	0.449	0.7200	1.206
PMS	0.424	0.6997	0.573
TMS	0.415	0.6922	0.292

* Approximate length of silane instead of organosilyl group on surface of the silica.

ular skeleton of a silane modifier can be estimated from known bond lengths (C–C, 0.155 nm; Si–C, 0.189 nm; Si–Cl, 0.203 nm), which is in good agreement with the experimentally determined thickness of the corresponding silane layer[6]. The calculated steric parameters are summarized in Table III.

Although the silane molecular length spans a wide range, from 0.292 to 2.472 nm, the A_m and B values vary in only a narrow range (see Table III). The correlation between B and L is further plotted in Fig. 2, which exhibits a good linearity and can be expressed by the algebraic equation:

$$B = 0.03268L + 0.6826 \tag{19}$$

Eqn. 19 shows how the length of a silane quantitatively affects the maximum surface alkyl concentration.

It is well known that, during formation of a chemically bonded monolayer, the conversion is limited by the maximum number of active sites that are accessible to the silanizing reagent.

The customary consideration deems that the maximum surface concentration of silyl groups is determined by the cross-sectional area of a bonded silyl group, but this does not adequately explain the difference in surface silyl group concentration for silanes with different alkyl chain lengths. The size-exclusion concept is proposed to approach this point. Silanization may be regarded as a self-forming size-exclusion process and the maximum conversion would occur when the bonded silica reaches the state of complete size exclusion of further silane modifiers, regardless of their concentration and reactivity. This process may be visualized as a planting of highly uniform trees on a plot of land. As the density of silane trees increases, the planting slows down and will eventually stop if no more trees can get into the silica plot owing

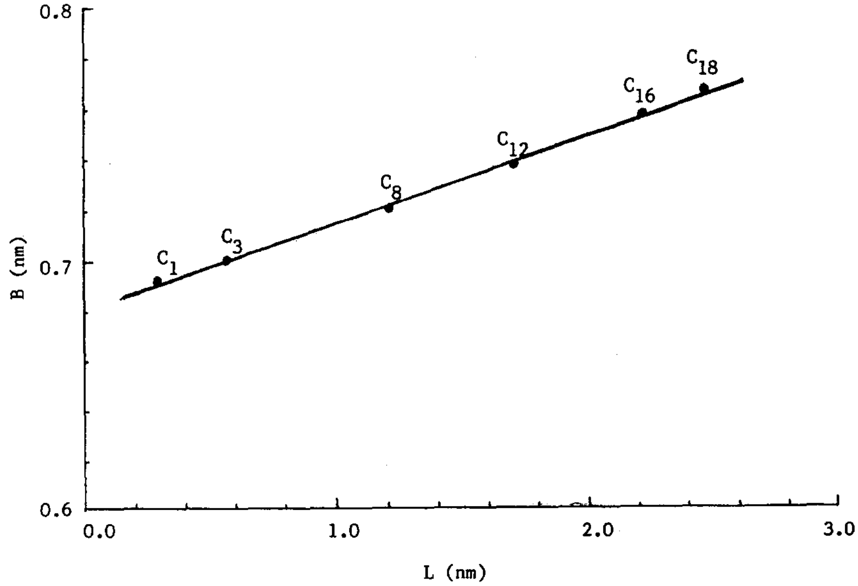

Fig. 2. The correlation between B and L. Points for C_{12} and C_{16} were calculated from eqn. 18.

to blocking by those already planted. Each kind of silane would possess a size-exclusion value, E, defined as the diameter of the minimum circular cross-section through which the silane can pass in a given set of reaction conditions.

If the silanes with the same E value were packed closely in a hexagonal arrangement on the silica surface, the B value would be equal to the E value. Otherwise B is always greater than E. However, the B values calculated from the experimental results are only slightly greater than 0.68 nm, which is the diameter of cross-sectional area for trimethylsilyl group calculated from Van der Waals radii[6]. This indicates that the bonded silyl groups on the silica surface are compactly packed, consistent with the previous postulation[1].

Hence the correlation between B and E can be expressed by the formula:

$$E = \psi B \tag{20}$$

where ψ is a coefficient with a value less than but close to 1. For a given surface property of silica and silylation conditions, ψ should be constant statistically.

For simplicity, ψ is assumed to be unity. The intercept in eqn. 19 represents the E value of dimethylchlorosilane (strictly speaking, this should be dimethylchlorosilyl), and the first term in the equation is the additional portion accounting for the chain-length effect. The silane molecule can be regarded as a rigid screw-shaped rod, and a rotation along its rod axis with a very small angle can be imagined.

Roumeliotis and Unger[1] mentioned that the n-alkyl chain bonded at the silica surface would have some freedom of rotational mobility, particularly when the chain was long. If this is true, the rotational effect of the bonded silane on the maximum alkyl surface concentration should also be taken into account.

Assuming that a bonded silane has a rotation angle, β, along its axis perpendicular to the silica surface, it would occupy a larger circular area than in the absence of rotation, and the difference in diameter would be $2L \cos \beta$, which would make a contribution towards the B value. Hence eqn. 19 should be rewritten as follows:

$$B = 0.6826 + kL + 2L \cos \beta \tag{21}$$

where k is a constant referring to chain-length effect on the size exclusion value, and $k + 2 \cos \beta = 0.03268$.

In the case of the composite phases, *e.g.* ODMS + TMS, eqn. 21, takes the form:

$$\bar{B} = 0.6826 + kL_1 + 2(1 - X)L_1 \cos \beta + 2XL_{18} \cos \beta \tag{22}$$

where $\bar{B}$ is the average for B_{18+1}, and X is the fraction of sites for ODMS, which can be calculated from α/α_t.

As mentioned before, the total alkyl surface concentration after endcapping is constant whatever the silane length in the primary silanization: in other words, the $\bar{B}$ values are same. Obviously, $\cos \beta$ should be zero for B (TMS) to be the same as $\bar{B}$ (ODMS + TMS).

Hence eqns. 21 and 22 reduce to the same form, *i.e.* eqn. 19. It may be concluded that a bonded silane on a silica surface in a good solvent such as toluene would stretch out perpendicularly from the surface and have little rotation freedom to affect the maximum alkyl surface concentration. This postulation is consistent with the conformational analysis of the close bonded silanes inasmuch as the rotation would result in a much higher intra- and interconformational energy.

Clearly, the E value is the critical parameter of a silane, governing the maximum alkyl surface concentration. Under multiple silanization conditions, *i.e.* stepwise bonding with different silanes, the silane with the smallest E value would determine the maximum silyl surface concentration.

It is interesting to note that, by some mathematical approximations (see Appendix), eqn. 19 can be transformed into the following form:

$$\alpha = 4.1149 - 0.394\,L \tag{23}$$

Eqn. 23 is very similar to eqn. 18, except that the variable is L instead of n. The n value for n-alkyl-dimethylchlorosilane is roughly proportional to L for the rigid rod molecular configuration. Hence eqn. 18 might reflect experimental phenomena but eqn. 23 should show the intrinsic nature. Strictly speaking, eqn. 19 would give a more accurate and non-linear relation between silane length and the corresponding maximum silyl surface concentration.

It has been noted that the primary alkyl surface concentrations obtained in the present study differ considerably from those reported by Roumeliotis and Unger[1]. A detailed comparison is listed in Table IV. The specific surface area determined by the BET method can be in error by up to 5% and may result in certain variations in the alkyl surface concentration. In order to eliminate this inaccurate factor, the ratio of an alkyl surface concentration to a TMS surface concentration is used. Obviously the ratios in the present study are significantly higher than the corresponding one from Roumeliotis and Unger's data.

There are two factors other than the E value that affect the alkyl surface concentrations under the same reaction conditions.

The original hydroxyl surface concentration and its distribution exert an influence on the alkyl surface concentration. For instance, if the B value between two

TABLE IV

COMPARISON OF ALKYL SURFACE CONCENTRATIONS

Modifier	*Roumeliotis and Unger's data*		*Present results*	
	µmole/m²	*Percentage of value for TMS*	*µmole/m²*	*Percentage of value for TMS*
ODMS	–	–	3.259	81.5
HDMS*	2.36	70.2	3.304**	82.6
OTMS	2.71	80.4	3.700	92.5
BMS***	2.97	88.1	3.880**	97.0
PMS	–	–	3.919	98.0
TMS	3.37	100	4.000	100

* Hexadecyldimethylchlorosilane.
** Calculated from eqn. 18.
*** Butyldimethylchlorosilane.

adjacent original hydroxyl groups is greater than the E value of a modifier, the alkyl surface concentration will be equal to the original hydroxyl surface concentration and lower than that it should be. In this case the heterogeneity of hydroxyl groups will further lower the alkyl surface concentration owing to some of the above mentioned B value being smaller than the E value. In other words, the heterogeneity will decrease the ψ value so as to increase the B value of the bonded silanes. However, at sufficiently high hydroxyl surface concentrations the heterogeneity would have little influence on the alkyl surface concentration, *i.e.* it would approach the statistical maximum, which should be a constant, and the E value will be the sole factor determining the alkyl surface concentration on the accessible surface. Fully hydroxylated silica has a hydroxyl surface concentration of 8–9 μmole/m^2 with a similar heterogeneity, so that it should give the same alkyl surface concentration for certain E values provided the total surface area is accessible for the silane molecules.

As mentioned in the literature[6], the pore size of the silica will have an effect on the alkyl surface concentration, depending on the ratio of the pore diameter to the size of a modifier molecule. Using the size-exclusion concept, there are two cases:

(a) If $D < 2L + E$ (D is the pore diameter), the silane molecules would mainly react at the pore opening region and block the remaining pore space so as to result in a considerably lower alkyl surface concentration.

(b) If $D > 2L + E$, the silane molecules could generally enter the inner pore space in spite of the reduction of the pore diameter caused by bonded silanes. However, in the case of $L > E$ and $D < 3L$, there may be still some steric hindrance in orienting the silane molecules to the pore walls, which would result in a slightly lower alkyl surface concentration.

The silica used in the present experiment had $D_{\max} = 8.5$ nm with $S_{\mathrm{BET}} = 160$ m^2/g (Sears' titration gives a specific surface area equivalent to S_{BET}). In contrast, the silica in Roumeliotis and Unger's experiment had $D_{\max} = 13.4$ nm with $S_{\mathrm{BET}} = 376$ m^2/g: the high specific surface area indicates that there must have been a considerable amount of micropores in their silica, which would result in a low local alkyl surface concentration for long-chain silanes.

The experimental α value is virtually the average alkyl surface concentration and can be expressed by the formula:

$$\alpha = \frac{\sum \alpha_i S_i}{S} \tag{24}$$

where α_i is local alkyl surface concentration for a certain pore size and S_i is the corresponding specific surface area; S is total specific surface area. This equation probably explains why the ratio of α to α_{TMS} would have different values for the same silane but different silicas. Conceivably the silanization without any pore hindrance would give the maximum α values for silanes with various chain lengths, which in turn give rise to a maximum ratio of α to α_{TMS}. Since it is hard to avoid micropores entirely in the formation of chromatographic silica, the maximum long-chain alkyl surface concentration as well as its ratio to α_{TMS} are best determined on non-porous silica. It may be expected that the differences of A_{m} and B values between long-chain silanes and TMS would be further reduced on non-porous silica.

CONCLUSIONS

Although the chosen surface pattern is simplified and does not represent the real surface, it is still a useful model for the analysis. On the basis of the experimental results and analysis, the following conclusions can be drawn.

(1) The alkyl surface concentration of primary silanization decreases linearly with an increase in the chain length of an *n*-alkyldimethylchlorosilane (eqn. 18).

(2) The total alkyl surface concentration after endcapping remains a constant regardless of the difference in primary silanization. In other words, the total alkyl surface concentration is determined by the silane with the shortest chain length.

(3) The sum of total alkyl surface concentration and the residual hydroxyl surface concentration is equal to the original hydroxyl surface concentration using low-temperature silanization.

(4) In the case of the completely accessible surface of a fully hydroxylated silica without physisorbed water, the alkyl surface concentration should be the same for a given silane under the same silanization conditions. However, the average alkyl surface concentration is dependent on the actual pore structure of a silica, especially the micropores. This indicates a heterogeneity of the bonded silane layer on silica surface.

(5) The size-exclusion principle and the rigid-rod molecular configuration for silanes appear to constitute a reasonable model for interpreting the steric effect of the chain length on silanization.

APPENDIX

Based on the assumption of hexagonal close packing, the correlation between A_m and B is as follows:

$$A_m = B^2 \sin 60^\circ \qquad \text{(A1)}$$

Note also that the relation between A_m and α is:

$$\alpha = 1/(A_m N) \qquad \text{(A2)}$$

where N is Avogadro's constant.

Now, B can be expressed by the formula:

$$B = FL + G \qquad \text{(A3)}$$

where $F = 0.03268$ and $G = 0.6826$. These three equations can be combined:

$$\alpha = \frac{1}{N \sin 60^\circ (FL + G)^2} \qquad \text{(A4)}$$

After binomal expansion eqn. A4 becomes:

$$\alpha = \frac{1}{N \sin 60^\circ (F^2L^2 + 2FGL + G^2)} \qquad \text{(A5)}$$

Since FL is much smaller than G the square of this term can neglected:

$$\alpha = \frac{1}{N \sin 60^\circ (2FGL + G^2)} \tag{A6}$$

After some manipulation, eqn. A6 can be expressed in the following form:

$$\alpha = \frac{1}{2NFG \sin 60^\circ} \left(\frac{2F}{G} - \frac{2FL}{G(L + 0.5G/F)} \right) \tag{A7}$$

If the L value is rather small (as in the case of surface silylation) so that $L \ll 0.5G/F$, eqn. 7 can be further approximated as follows:

$$\alpha = \frac{1}{NG^2 \sin 60^\circ} - \frac{2F}{NG^3 \sin 60^\circ} L \tag{A8}$$

Inserting the numerical values of N, F and G into eqn. A8, one finally obtains:

$$\alpha = 4.1149 - 0.394L \tag{A9}$$

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REFERENCES

1 P. Roumeliotis and K. K. Unger, *J. Chromatogr.*, 149 (1978) 211–224.
2 J. B. Crowther, S. D. Foizio, R. Schiksnis, S. Marcus and R. A. Hartwick, *J. Chromatogr.*, 289 (1984) 367–375.
3 F. Cisenbesiss and K. F. Krebs, *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, 1977*, paper No. 311.
4 G. W. Sears, *Anal. Chem.*, 12 (1956) 1981.
5 J. J. Kirkland, *Chromatographia*, 8 (1975) 661–668.
6 K. K. Unger, *Porous Silica — Its Properties and Use as Support in Column Liquid Chromatography*, Elsevier, Amsterdam, New York, 1979.
7 T. Welsch and H. Frank, *J. Chromatogr.*, 267 (1983) 39–48.
8 H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry*, Prentice-Hall, New Jersey, 1981, pp. 448–481.
9 C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1967, Ch. 2.