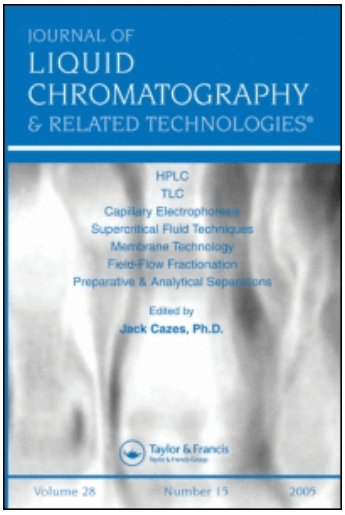

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THE EFFECT OF THE REACTION MEDIUM ON THE COVERAGE DENSITY OF C_{18} CHEMICALLY BONDED PHASE+

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ABSTRACT

A wide-pore silica for HPLC (S_{BET}= 360 m^2 g^{-1}, D = 20 nm, V_p = 2.1 cm^3 g^{-1}) was silanized with n-octadecyl dimethylchlorosilane in the presence of several base activators. It has been found that the density of bonded octadecyl ligands is not only a function of re-

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action time and temperature, but also depends upon the structure of the organic base used as reaction activator. The reproducible synthesis of silica bearing more than 4 /umol m^{-2} of octadecyl ligands is described.

INTRODUCTION

Commercially available organochlorosilanes are most often used in synthesis of alkyl-modified silica for reversed phase liquid chromatography (RPLC). Recently, we have found that this reacrion is a reversible one in a closed reaction system [1, 2].

$$R_2\text{-}\underset{R_3}{\overset{R_1}{\underset{|}{\overset{|}{Si}}}}\text{-Cl} + \equiv Si\text{-}OH \rightleftharpoons \equiv Si\text{-}O\text{-}\underset{R_3}{\overset{R_1}{\underset{|}{\overset{|}{Si}}}}\text{-}R_2 + HCl \qquad (1)$$

The presence of HCl in reaction system therefore does not enable to achieve high ligand densities. The same situation was observed with alkoxysilanes. On the other hand, the reaction or silica with aminosilanes yields silica surfaces covered densely with alkyl ligands (> 4 /umol m^{-2}) [1-6].

To enhance the silanization of silica with chlorosilanes, hydrogen chloride evolved in the course of reaction (eq.(1)) is neutralized with a suitable organic base (activator - A) added to reaction mixture, e.g. pyridine [7]. The role of solvent and base activator was discussed by several authors [1,8,9]. Unger et al.[9] have shown that the base does not only neutralize free

HCl, but also acts as a catalyst of the silanization. The catalytic action of base activators is explained by complexation between organic bases and chlorosilanes. The latter compounds are well known to form stable complexes with e.g. pyridine, quinoline, formamide, dimethylformamide, acetamide or tertiary amines (see literature given in ref. [10]).

The aim of the present work was to study in detail the role of base activators. Several organic nitrogen bases with varying structure and basicity was chosen for this purpose.

EXPERIMENTAL

Materials and reagents

One batch of wide-pore silica [11,12] was used through silanization experiments. n-Octadecyldimethylchlorosilane (ODMCS) was used as obtained from Petrarch Systems,(Levittown, Pa, USA). Hexamethyldisilazane was purchased from Lachema (Brno, Czechoslovakia) as well as all the solvents used; toluene being a reaction medium in silanization experiments was dried especially [13]. The organic bases obtained from various sources were in-glass distilled before use. The content of water in solvents and activator was checked by means of Karl Fischer reaction.

Surface modification

In a glass ampoule, a constant amount of bare silica (5 grams) was dried at 10 Pa and 200°C for 6 hours. ODMCS (12.5 - 25 mmol), 20 ml of dry toluene and 25 - 37.5 mmol of activator were added to the silica. The ampoules were sealed and heated at 100 - 130°C for 6 hrs. After the silanization, the reaction solution was removed and resulting silica was washed with 50 ml of dry toluene, methanol and dimethylether. Before physicochemical measurements, the samples were dried under vacuum at room temperature for 24 hrs.

Physicochemical measurements

The specific surface area (S_{BET}), mean pore diameter (D) and pore volume (V_p) of the starting and silanized silica were determined with Sorptomatic 1800 (Carlo Erba, Milano, Italy).

The concentration of silanols before and after silanization was determined by means of their reaction with a complex of dimethylzinc with tetrahydrofurane [14,15].

The surface density of octadecyl ligands (α_{RP}) was determined accordingly Berendsen et al.[16]; the content of carbon was determined with Elemental Analyser 240 (Perkin Elmer, Norwalk, USA). Secondary silanizstion of samples with HMDS was carried out using procedure reported earlier [17].

RESULTS AND DISCUSSION

In Table 1, the activators used are summarised. We have found that reaction time longer than 8 hrs does not influence the yield of silanization in the presence of activators. In absence of activator, the silanization was found to be evidently slower.

In Fig. 1, two kinetic curves are compared to demonstrate the accelerating effect of activator. On the other hand, a variation in ODMCS concentration has only a minor effect at a sufficient excess of ODMCS.

TABLE 1

Organic bases used as activators

Sample number	Denotation	Activator (A)	Formula	pK_a [x]
1		bare silica gel		-
2	▲	quinoline		4.80
3	◑	pyridine		5.25
4	●	morpholine		8.33
5	△	N-methylpyrrolidone		10.60
6	■	piperidine		11.12
7	□	2-pyrrolidone		11.26
8	○	none		-

[x] data from ref.[18].

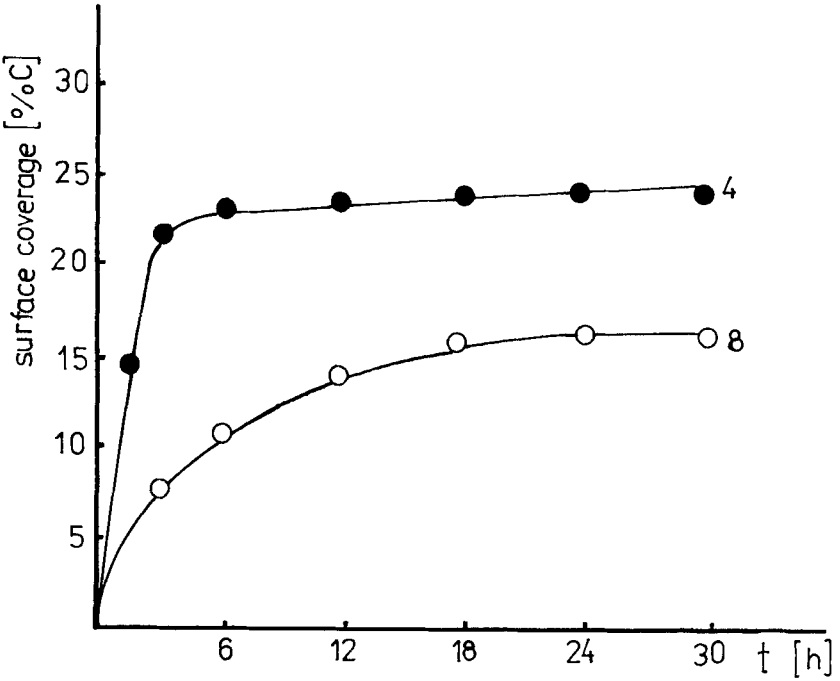

Fig 1. Percentage of carbon bonded versus reaction time / t /. Symbols denoted in Table 1.

TABLE 2

Physicochemical characteristics of the studied sorbents

Sample number	S_{BET} m^2/g	V_p ml/g	D nm	Sueface coverage		
				%C	α_{RP} /umol/m^2	α_{SiOH} /umol/m^2
1	360	2.1	20.0	-	-	5.21
4	175	1.5	14.3	24.5	4.21	0.53
8	226	1.75	16.7	15.6	2.28	2,90

The physicochemical characteristics of the resulting sorbents (sample 4 and 8) are given in Table 2

It has been found that an optimal ratio of silane to activator exist for every base.

In Fig. 2, the activating effects of morpholine and pyridine are compared under identical reaction conditions. It must be however emphasized that two distinct groups of activators have been used:

a) secondary amines which are capable of in situ formation of reactive aminosilanes,

b) tertiary amines or azaaromatics forming addition complexes with chlorosilanes.

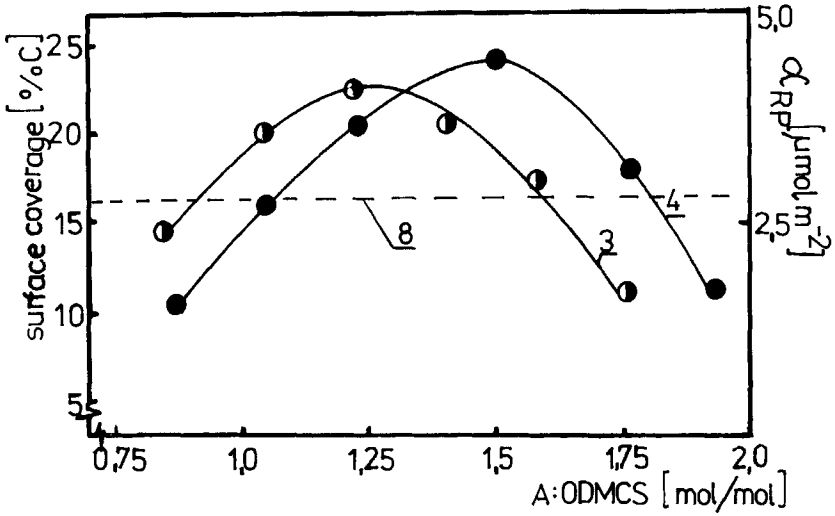

Fig 2. Effect of addition and basic properties of activator on coverage density of support's surface by C_{18} chemically bonded ligands, 3 - pyridine, 4 - morpholine, 8 - without activator.

We have found that the optimum concentration of activator depends upon its basicity. The existence of such optima could be explained on the base of following reaction scheme:

$$\text{Silane} + \text{Base} \rightleftharpoons \text{Intermediate} \quad (2)$$

$$\text{Si-OH} + \text{Intermediate} \rightleftharpoons \text{Si-O-ligand} + \text{Base}\cdot\text{HCl} \quad (3)$$

$$\text{Si-OH} + \text{Base} \rightleftharpoons \text{Si-OH}\cdots\text{Base} \quad (4)$$

In steps (2)-(4), the equilibrium depends upon the basicity of activator given as pK_a. Activator forms an intermediate or complex with chlorosilane but also blocks free, unreacted silanol groups. The blocking effect as well as the binding of HCl increases with increasing basicity of activator. For strong bases the interaction with silica is irreversible, e.g. for 2-pyrrolidone ($pK_a = 11.26$) 2.13% of N was found in silanized silica after silanization and solvent treatment.

Thus, optimal reaction conditions can be found for every activator (Table 3).

This enabled us to change the density of octadecyl ligands in a reproducible way. Comparing our experimental date obtained for various activators of the both groups, an optimal range of pK_a (7 - 9) is found (see Fig. 3) to obtain a high ligand density ($\alpha_{RP} > 4$ /umol/m^2). Thus, $\alpha_{RP} = 4.21 \pm 0.1$ /umol/m^2 was achieved with morpholine ($pK_a = 8.3$). This is in accord with recent results of Kinkel and Unger [9] who recommended immidazole (pK_a =

TABLE 3

Surface concentration of the chemically bonded C_{18} groups

Number of sample	Surface coverage			Concentration SiOH		A:ODMCS ratio mol/mol
	%C	α_{RP} /umol/m^2	α_{RP} after end-capping	α_{SiOH} µmol/m^2	α_{SiOH} after end-capping	
1	bare silica gel			5.21		
2	21.36	3.41	4.39	1.14	0.77	1.25:1
3	22.51	3.68	4.32	0.72	0.68	1.25:1
4	24.54	4.21	4.28	0.53	0.39	1.50:1
5	20.77	3.27	4.59	1.78	0.61	1.50:1
6	19.64	3.04	4.62	2.26	1.04	1.00:1
7	17.80	2.55	4.79	2.42	1.27	1.00:1
8	15.55	2.28	5.01	2.94	2.07	-

6.97) as a substance " catalysing " silanisation of silica with monochlorosilanes in an optimal way. It must be however stressed that additional steric effects are supposed to influence the silanisation reaction as it has been discussed earlier.

The secondary silanization of sorbents (endcapping) with HMDS causes an additional increase in the carbon content (Table 3). A remarkable increase is observed for samples with low density of octadecyl ligands. In the case of extremely dense coverage obtained e.g. with

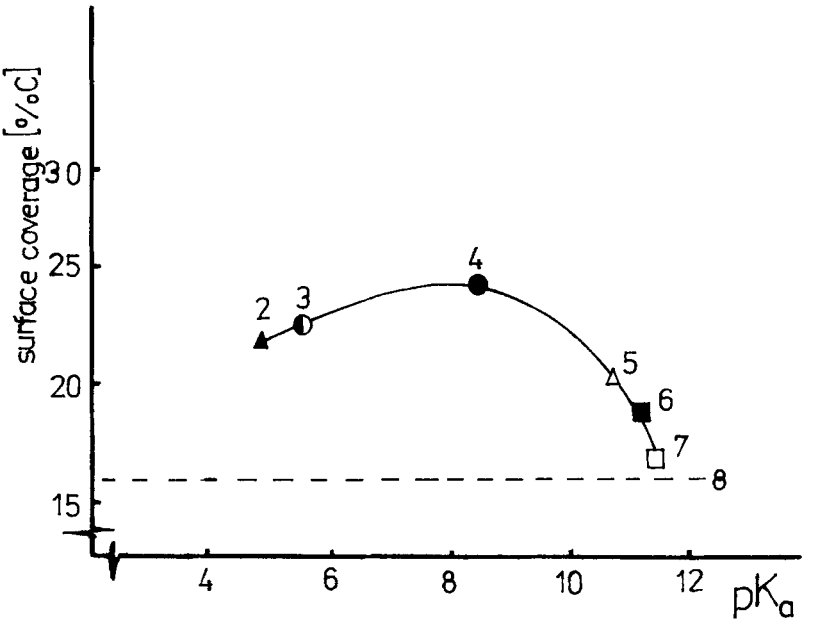

Fig 3. Effect of the pK_a values on the surface coverage. Symbols denoted in Table 1.

morpholine (Sample 4), only negligible change in carbon content was measured. Thus, the ligand density obtained at optimal conditions is comparable with that observed previously in silanization of wide-pore (Table 3) silica with N,N-dimethylaminooctadecylsilane [1-5].

CONCLUSIONS

We may conclude that the silanization of bare silica with chlorosilanes in the presence of base reaction activators enables to achieve high ligand densities if a wide-

pore silica with sufficient concentration of silanols (α_{SiOH} 5.0 /umol/m^2) is used. The presence of base activator in reaction mixture increases the rate of silanization as well as the final density of bonded ligands. The ligand densities obtained at optimal conditions are similiar to that obtained with octadecyldimethyl N,N-dimethylamino-silane with the same silica gel. However, the reaction rate of silanization was higher in case of the silanization activated with organic bases. The method gives reproducible ligand densities by changing of the concentration of the base activator.

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