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Silanol effects in reversed-phase liquid chromatography

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SUMMARY

A large number of butyl-, hexyl-, octyl- and octadecylsilica stationary phases were synthesized by the usual low-temperature and also novel high-temperature silylation methods. The phases were characterized by measuring their silanol concentrations, organic functional group concentrations and wettabilities and, additionally, by reversed-phase liquid chromatographic retention measurements. Unusual retention data, not expected on the basis of the solvophobic retention theory, were observed and are explained. Separation selectivity and peak asymmetry are interpreted by taking into account the surface concentrations of both the silanol groups and the organic functional groups. The peak shape is better, but the separation selectivity is lower, when access to all silanol groups of a stationary phase is equally easy or equally difficult.

INTRODUCTION

Silica-based reversed-phase materials are the most frequently used high-performance liquid chromatographic (HPLC) stationary phases today. The reproducible production of reversed-phase silicas is still a challenge owing to our incomplete understanding of the relationships between the properties of the parent silica, the type and conditions of the derivatization reaction, the type and characteristics of the resulting surface and its chromatographic behaviour^{1–3}. As surface derivatization is never complete, one always has to consider the effects of the underivatized silanol groups, particularly their undesirable characteristics such as unpredictable retention order changes, tailing of certain polar solutes and low recovery rates of basic solutes^{1–5}.

It has been observed that end-capping with small silane reagents can eliminate some of the problems commonly attributed to the underivatized (or “residual”) silanol groups. For most reversed-phase silicas the true surface concentration of the unreacted silanol groups is unknown, and it is assumed to be equal to the difference between the original silanol concentration and the surface concentration of the bonded alkyl

groups. Often, in studies dealing with the effects of the residual silanol groups and seeking a correlation with the observed chromatographic behaviour the conclusions are based mainly on the surface concentration of the organic functional groups. Also, fairly often, end-capped and non-end-capped materials are compared directly⁶⁻¹⁰, resulting in limited, qualitative conclusions.

We have developed a high-temperature silylation process that allowed us to prepare reversed-phase materials on which the surface concentration of the organic functional groups is high and that of the residual silanol groups is low^{11,12}. Using both this and the "regular" low-temperature silylation method¹³, we were able to produce a large number of reversed-phase packing materials with different residual silanol group and organic functional group concentrations^{11,12,14}. These materials were used in this study, in which the influence of the silanol group concentration on solute retention, selectivity and peak shape were investigated for polar test solutes using methanol-water eluents. These studies complement our previous investigations of the same stationary phases with *n*-heptane as eluent¹⁵.

EXPERIMENTAL

Physico-chemical characterization of the silicas

The silica starting material and the reversed-phase packings synthesized from it were characterized by nitrogen adsorption (BET) surface area measurements (S_{BET}). Pore-size distribution and pore-volume data were derived from the S_{BET} values^{12,14}. Elemental analysis was used to determine the surface concentration of the organic functional groups (A_{C}). The reaction of methylolithium with silica¹⁶ was used to determine the surface concentration of the silanol groups (A_{OH})^{11,14,17}. As discussed previously¹⁷, the relative standard deviation of this method is 7% for Si 100 silica and 5% for RP-10 silica (five measurements).

Preparation of the stationary phases

The principles and reaction conditions of the high-temperature silylation method used for the preparation of some of the materials studied here are described elsewhere^{11,12,14}. All stationary phases were synthesized from a single batch of LiChrosorb Si 100 silica (Merck, Darmstadt, F.R.G.). This silica was selected because the pH of its aqueous slurry is nearly neutral^{18,19} and its surface is fully hydroxylated (see below).

To characterize the silica batch, its pH was measured by suspending 10 mg of silica in a mixture of 0.5 g of isopropanol and 0.5 g of 0.2 *M* aqueous potassium nitrate. The pH of the slurry¹¹ was 5.67. The specific surface area, S_{BET} , of the silica batch was 257 m²/g, and its pore volume, V_{p} , was 1.31 ml/g. Prior to silylation, LiChrosorb Si 100 was vacuum dried (0.2 Torr) at 180°C for 2 h to remove the physisorbed water. The silanol content of the dried material, A_{OH} , was determined to be 2250 $\mu\text{mol/g}$, which corresponds to a surface silanol concentration of 8.7 $\mu\text{mol/m}^2$, which agrees very well with results given in the literature for fully hydroxylated silicas^{13,20}.

The silylating reagents di-*n*-hexyltetramethyldisilazane (DHTMDS) and di-*n*-octadecyltetramethyldisilazane (DOTMDS) were synthesized in our laboratory^{11,14}. Their structure and purity were characterized by gas chromatography-mass spectrometry and NMR spectroscopy. The reagents contained a total of *ca.* 10% of the

corresponding silylamines and disiloxanes as by-products. Hexamethyldisilazane (HMDS) was obtained from Fluka (Buchs, Switzerland), and used as received. All other solutes and solvents were of analytical-reagent grade or better and were obtained locally from a number of sources. They were dried prior to use.

The preparation methods and some of the main characteristics of the reversed-phase materials studied are listed in Table I. RP silicas RP-6 I–III and RP-18 I–III were prepared by reacting the silica at room temperature with a *m*-xylene solution of the respective disilazane for 4–120 min. For 1 g of LiChrosorb Si 100, 40 ml of a 0.2 *M* solution of the disilazanes in *m*-xylene were applied. RP-6 IV and RP-18 IV were prepared by refluxing 5 g of LiChrosorb Si 100 in 200 ml of a 0.25 *M* disilazane solution in *m*-xylene for 12 h.

To achieve a very weak end-capping effect, materials RP-6 IV and RP-18 IV were allowed to stand at room temperature in HMDS solution (40 ml of 0.2 *M* HMDS in *m*-xylene for 1 g of RP silica) for 1 h, yielding materials RP-6 V and RP-18 V. The same procedure was applied overnight to RP-6 IV, resulting in material RP-6 VI.

To achieve more complete end-capping, RP-6 IV and RP-18 IV were refluxed at 139°C for 8 h in the HMDS solution, yielding materials RP-6 VII and RP-18 VII.

Materials RP-6 VIII–X and RP-18 VIII and IX were prepared by high-temperature silylation^{11,12,14}. These reactions were carried out in a thick-walled glass ampoule (15 cm × 2 cm I.D.). Disilazane (0.01 mol) was added to the tube and a filter-funnel holding 1 g silica was placed into the ampoule. The ampoule, cooled in dry-ice-acetone and kept in a vertical position, was flushed with dry nitrogen and flame-sealed. The ampoule was then placed vertically in a gas chromatographic oven and heated at a rate of 4°C/min to the final temperature and held there for 12–15 h. The final temperatures were 220°C for RP-6 VIII, 270°C for RP-6 IX, 320°C for RP-6 X and RP-18 X and 360°C for RP-6 XI and RP-18 XI. The ampoules were then slowly cooled to ambient temperature and opened.

All materials were washed by the same procedure, consisting of two rinses with 30 ml each of toluene, dichloromethane and acetone per gram of silica. Finally, the materials were dried under vacuum at 80°C for 4 h.

Wettability tests

The wettability of the reversed-phase materials in methanol–water mixtures was determined according to Engelhardt and Mathes²¹. A 100-mg amount of the stationary phase was mixed with 25 ml of water in an erlenmeyer flask. While shaking the flask, methanol was added dropwise to the slurry until the modified silica particles that floated on the surface had sunk to the bottom. At this point the surface tension of the liquid, σ_l , and the critical surface energy of the reversed-phase silica, σ_s , were considered to be equal. Based on experimental data²², a relationship was obtained between the composition of the liquid and its surface tension as:

$$\log \sigma_s = \log 166.3 - 0.406 \log [\% (v/v) \text{ methanol}] \quad (1)$$

where σ_s is in mN/m and the methanol concentration can vary between 15 and 85% (v/v). Although the critical surface energy values thus obtained may be subjectively biased, they nevertheless permit a reasonable comparison of the synthesized phases.

TABLE I
PREPARATION CONDITIONS AND MAIN CHARACTERISTICS OF THE REVERSED-PHASE MATERIALS USED

Phase symbol	Reaction conditions	RP-6			RP-18		
		α_c ($\mu\text{mol/g}$)	α_{OH} ($\mu\text{mol/g}$)	Wettability ^a	α_c ($\mu\text{mol/g}$)	α_{OH} ($\mu\text{mol/g}$)	Wettability ^a
I	Room temp., 4 min shaking	278	1784	25	126	1865	25
II	Room temp., 60 min shaking	305	1692	25	229	1722	25
III	Room temp., 120 min shaking	339	1463	41	277	1654	29
IV	Reflux in <i>m</i> -xylene, 12 h	790	1040	51	756	949	56
V	End-capping IV with HMDS at room temp., 1 h	714	989	48	764	826	57
VI	End-capping IV with HMDS at room temp., overnight	673	798	52	NP ^b	NP	NP
VII	End-capping IV with HMDS by refluxing at 139°C, 8 h	622	482	53	743	528	59
VIII	High-temp. silylation at 220°C	971	421	53	NP	NP	NP
IX	High-temp. silylation at 270°C	995	264	57	NP	NP	NP
X	High-temp. silylation at 320°C	830	190	57	NP	NP	NP
XI	High-temp. silylation at 360°C	1013	155	59	582	377	64
					512	275	63

^a Wettability: methanol (% v/v) in aqueous eluent required to wet the phase.

^b NP = Not produced.

Chromatographic measurements

The reversed-phase materials were slurry packed into 4 and 1.2 mm I.D. stainless-steel columns of different lengths²³. Most of the measurements were carried out with a liquid chromatograph assembled from commercially available parts: an L5000 gradient unit, an L655A12 pump, an L655A22 UV detector and D2000 integrator (all from Merck-Hitachi, Darmstadt, F.R.G.). Capacity factor measurements were made in the elution mode using 50 nM sample solutions. All columns were carefully thermostated²³ at 23°C. The retention data used here are the averages of several duplicate determinations (minimum five). Only retention data with less than a 1% relative standard deviation are used throughout the paper. The column dead volume was determined with deuterium oxide. Peak asymmetries were calculated from peak-width measurements at 15% of the peak height using the equation

$$As = 100 b_{15}/a_{15} \quad (2)$$

where a_{15} and b_{15} are the distances between the peak apex and the ascending and descending parts of the peak, respectively.

RESULTS AND DISCUSSION

Retention vs. surface composition relationships

Two RP-6 stationary phases, RP-6 IV and RP-6 X, which have nearly identical organic group concentrations but very different unreacted silanol concentrations (see Table I), were selected for the retention studies. The capacity factors of benzene, phenol and hydroquinone as a function of the methanol concentration of the eluent are shown in Fig. 1. The capacity factors of two crown ethers, 18-crown-6 and 12-crown-4, are shown in Fig. 2.

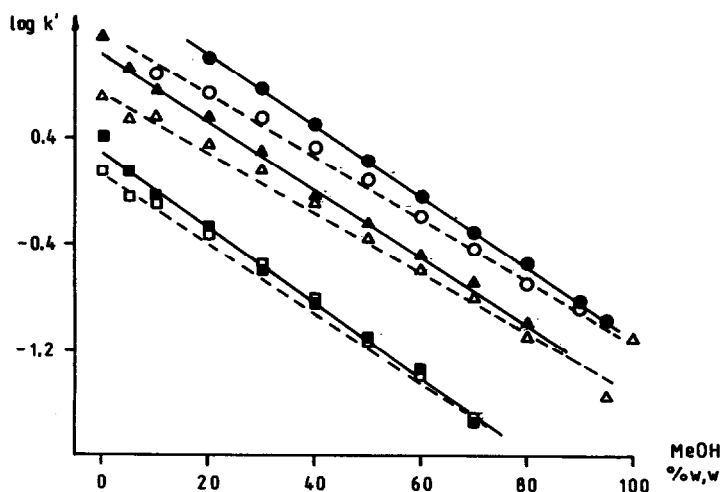


Fig. 1. $\log k'$ as a function of the eluent composition on RP-6 reversed-phase silicas. Open symbols, $A_C = 790 \mu\text{mol/g}$, $A_{OH} = 1040 \mu\text{mol/g}$; full symbols, $A_C = 830 \mu\text{mol/g}$, $A_{OH} = 190 \mu\text{mol/g}$. \circ , \bullet = Benzene; Δ , \blacktriangle = phenol; \square , \blacksquare = hydroquinone. MeOH = Methanol.

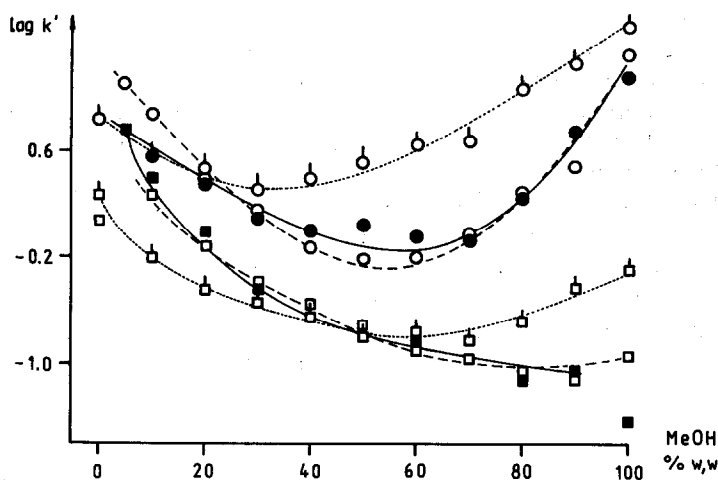


Fig. 2. $\log k'$ as a function of the eluent composition for (○, ●) 18-crown-6 and (□, ■) 12-crown-4. Dotted lines, parent silica; broken lines, RP-6 IV; full lines, RP-6 X.

The two classes of solutes show very different retention behaviours. In Fig. 1 the $\log k'$ values of all solutes decrease linearly with increasing methanol concentration in the eluent. As the polarity and water solubility of the solutes decrease from that of hydroquinone to benzene, the solute retention increases. The slope of the lines is slightly lower for the silanol-rich material. This behaviour is adequately explained by the simple solvophobic retention theory of Horváth *et al.*²⁴.

However, the $\log k'$ vs. methanol concentration curves shown in Fig. 2 are non-linear. To account for such a behaviour, Horváth and co-workers^{5,25} introduced the "dual retention mechanism" concept. The measured k' values, which passed through a minimum as a function of the water concentration of the eluent, were perceived to represent the sum of the hydrophobic capacity factor contribution and the hydrophilic capacity factor contribution.

The $\log k'$ of 18-crown-6 has an unequivocal minimum point, whereas the $\log k'$ vs. methanol concentration relationship for 12-crown-4 is merely curved. It is interesting that the retention curves are nearly identical on both the silanol-rich and the silanol-poor reversed-phase materials. The small retention differences cannot be explained solely by Horváth and co-workers' dual retention mechanism model, because the silanol concentrations (A_{OH} values) are very different, being 1040 and 190 $\mu\text{mol/g}$, respectively. This means that the crown ethers also behave as do the weakly polar solutes shown in Fig. 1, and cannot very well sense the large differences in the silanol concentration of the surface.

The non-linear retention behaviour must be caused by at least one other effect, such as the solvation (and conformational) changes of the crown ethers in the liquid phase that are induced by changes in the methanol concentration. This hypothesis may perhaps be substantiated by the observed proton NMR shifts of crown ethers in deuterium oxide-perdeuterated methanol mixtures. The chemical shift of the proton signal of 18-crown-6 varies almost linearly with the methanol concentration; it moves from 3.55 ppm in pure perdeuterated methanol to 3.97 ppm in pure deuterium oxide.

These shifts indicate that indeed there is a conformational change. This conformational change in turn might affect the retention of these solutes, and explain the observed retention curves.

In a previous paper¹¹ we described the irregular retention behaviour of aniline and pyridine on two RP-6 stationary phases with different silanol group concentrations. Maximum curves were observed for the basic solutes. In order to discuss here these effects in detail, the k' values of aniline, pyridine and benzene are plotted as a function of the methanol concentration in Fig. 3. The $\log k'$ values of all three solutes decrease with increasing methanol concentration. However, reproducible retention irregularities can be observed in the 50–80% methanol concentration range for pyridine and aniline. These irregularities cannot be explained by the current forms of either the solvophobic retention theory²⁴ or the dual retention mechanism model^{5,25}. On the silanol-rich RP-6 IV material ($A_{OH} = 1040 \mu\text{mol/g}$) pyridine shows two local maxima, the first centred around 55% and the second around 68% methanol. These maxima are slightly shifted towards higher methanol concentrations on the RP-6 X material, which has a lower silanol concentration ($A_{OH} = 190 \mu\text{mol/g}$).

Our explanation for this irregular retention behaviour is based on the dynamic surface models^{26–29}, especially on that of Nikolov²⁹. These models stipulate that the surface of the reversed-phase material is not wetted when the water concentration of the eluent is high. The bonded organic groups “fold up” in these eluents and form a dense layer which is more or less impenetrable to the eluent constituents and the solutes. The hydrophobic–dispersive interactions between the solutes and the stationary phase occur at the surface of this folded ligand layer. As the methanol concentration is increased, the surface becomes wetted. Once wetted, both the solvent and the solute molecules can penetrate the ligand layer and interact with the bulk of the organic groups. Simultaneously, the previously shielded silanol groups become

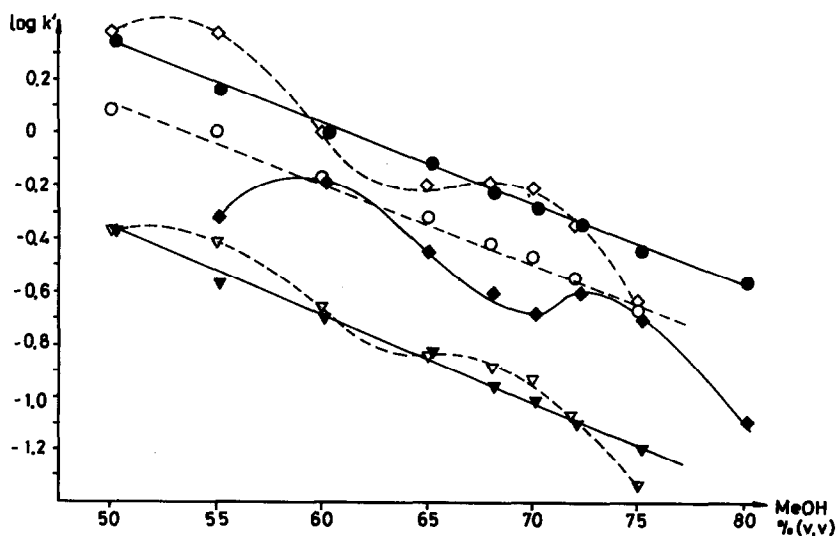


Fig. 3. $\log k'$ as a function of the eluent composition for (○, ●) benzene, (◇, ◆) pyridine and (▽, ▼) aniline. Broken lines, RP-6 IV; full lines, RP-6 X.

accessible and begin to contribute to the retention of the basic solutes, but not to the retention of benzene. As the methanol concentration is increased even further, a point is reached where all ligands become fully solvated, allowing full interaction with the silanol groups.

In order to support this interpretation of the experimental results, the wettabilities of the reversed-phase materials were determined. RP-6 IV, which has a high silanol concentration, is wetted by 51% methanol, whereas RP-6 X, which has a low silanol concentration, is wetted only at the 57% methanol concentration level (Table I). These values agree well with the points where k' begins to increase towards the first maximum shown in Fig. 3. Obviously, on the silanol-rich material the critical surface energy and the surface tension of the solvent mixture become numerically equal at lower methanol concentrations. This also explains why the position of the first k' maximum of pyridine is shifted towards higher methanol concentrations on the RP-6 X material: this phase contains fewer silanol groups and only eluents with higher methanol concentrations will wet it. The retention changes are so large that they result in retention order reversals for the benzene-pyridine peak pair. This observation is in agreement with the results of Engelhardt *et al.*³⁰, who reported that separation selectivities for the amines in general change strikingly when the composition of the eluent becomes equal to the composition of the methanol-water mixture which wets the reversed-phase material. The wettability data in Table I indicate that although the surface concentrations of the organic functional groups are similar on two reversed-phase materials, their wettabilities and hydrophobicities vary greatly with their actual silanol concentrations. When both the silanol and the organic functional group concentrations are comparable, the longer chains (C_{18}) require a higher methanol concentration for proper wetting.

Following Fowkes' treatment³¹, the surface energy of solids can be split into dispersive and polar parts:

$$\sigma_s = \sigma_s^d + \sigma_s^p \quad (3)$$

where σ_s is obtained from the wettability test and eqn. 1. The σ_s^d values can be approximated by the tabulated surface tension values of the analogous n -alkanes²², then the polar part, σ_s^p , can be calculated by eqn. 3. The calculated σ_s^d and σ_s^p values for the RP-6 IV and RP-18 IV phases are given in Table II. The polar part is much lower for the RP-18 IV phase, indicating that the longer chains have stronger shielding effects and that the influence of silanols is more pronounced when the stationary phase contains a shorter alkyl group. The apparent contradiction, which arises from the fact

TABLE II
SURFACE ENERGIES (mN/m) OF AN RP-6 AND AN RP-18 SILICA

Total surface energy, σ_s , of RP-6 and RP-18 silica divided into dispersive, σ_s^d and polar, σ_s^p parts.

Material	σ_s	σ_s^d	σ_s^p
RP-6	33	20	13
RP-18	32	28	4

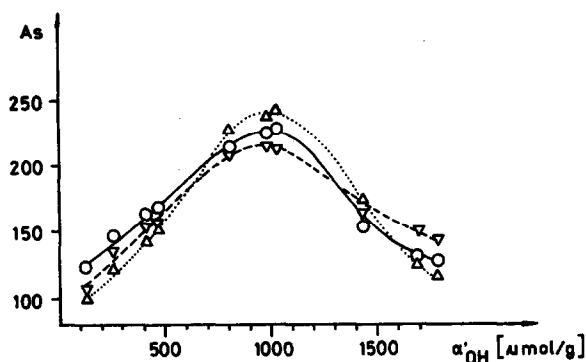


Fig. 4. Peak asymmetry as a function of the surface concentration of the silanol groups, A_{OH} , on RP-6 materials. For phase designations see Experimental. \circ = Benzyl alcohol; ∇ = phenol; \triangle = aniline. Mobile phase: methanol-water (65:35, w/w).

that in *n*-heptane eluents the shielding effect does not become stronger as the length of the alkyl chain is increased past the butyl group, can be resolved by noting that in *n*-alkane solvents the long alkyl chains are completely solvated and can move more freely.

Peak shape vs. surface composition of the alkylsilica stationary phase

As the unreacted silanol groups have been blamed for most of the undesirable effects on reversed-phase silicas, several attempts were made to eliminate them either by the use of special silane reagents², by end-capping with trimethylchlorosilane and/or HMDS or, occasionally, by adding polar masking agent to the eluent. However, a correct interpretation of the results was hampered by the fact that in most instances the actual silanol concentration of the phase was not known and quantitative correlations could not be obtained.

As we always determined the actual silanol concentration of each stationary phase by the methyllithium method (see Experimental), the peak shape and peak asymmetry data could be quantitatively correlated with the surface composition data. The asymmetry factors for the RP-6 and RP-18 phases are shown in Figs. 4 and 5,

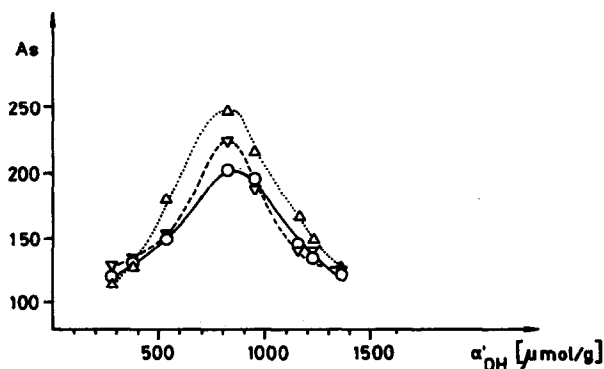


Fig. 5. Peak asymmetry as a function of the surface concentration of the silanol groups, A_{OH} , on RP-18 materials. For phase designation see Experimental. Symbols and mobile phase as in Fig. 4.

respectively. It is obvious that contrary to widely held beliefs, the asymmetry curves show a maximum when the silanol concentrations of the stationary phases are in the intermediate range (700–1100 $\mu\text{mol/g}$). These intermediate silanol concentrations are typical of the RP silicas that are produced under conditions widely accepted as optimum¹³.

As the alkyl group is changed from butyl to octadecyl, the maximum curve becomes sharper (it is spread over a narrower A_{OH} range)³². This explains why end-capping has such a large influence on the peak shape on octadecylsilicas without affecting appreciably the carbon content of the phase^{6–10}. It can be seen from Fig. 5 that the peak shape is excellent when the reversed-phase silica is deliberately incompletely derivatized (type I and II phases), a phenomenon noted, although quantitatively not explained, by Bidlingmeyer *et al.*³³ and Miller *et al.*³⁴. The peak asymmetry is worse on the regularly silylated RP-18 silicas that have a higher percentage of their silanol groups derivatized (type IV phases). Asymmetry, ironically, deteriorates even further as the material is treated with HMDS (type V material). Only when the silanol concentration is greatly reduced by drastic end-capping (type VII material) does the peak shape improve.

Very low silanol concentrations (type IX–XI materials) can only be achieved by high-temperature silylation^{11–13}. The peak asymmetries observed on these materials are as good as those on the silanol-rich materials. These findings imply that if one uses the dense monolayer-covered, commercially available RP-18 silicas, one must be willing to accept more or less severe peak asymmetry, which can be decreased only when appropriate masking agents are added to the eluents.

These findings also support the idea that it is not the absolute concentration of the silanol groups but rather their partially hindered accessibility that leads to, and controls, peak asymmetry².

Separation selectivity vs. surface composition of the alkylsilica stationary phase

The surface silanol groups of the alkylsilica stationary phases can, on the other hand, play a useful role as far as separation selectivity is concerned. In order to elucidate these effects, the relative retention values, r , with respect to benzene, of a number of polar solutes were determined on the different RP-6 phases. The representative results obtained with simple, strongly polar functional groups are shown in Fig. 6. Both the A_{OH} and the A_{C} values of the phases are shown on the horizontal axis. It can be seen that the most rapid change in selectivity occurs at intermediate silanol concentrations, in the 600–1000 $\mu\text{mol/g}$ range. (In the low to moderate silanol group concentration range, benzonitrile is an especially sensitive probe towards small changes in the silanol group concentration.)

Owing to the presence of fundamentally similar adsorption sites on the very hydrophobic stationary phases, the selectivity effects that are related to the polar functional groups of the solutes are mostly lost. On the silanol-rich materials the retention of all kinds of solutes is low. Only appropriate chemical modification of the surface, resulting in the presence of more than one type of adsorption site, can change both the topology and the adsorption energy distribution of the surface^{35–37} and result in a large polar separation selectivity. This, unfortunately, will also effect the peak asymmetry values.

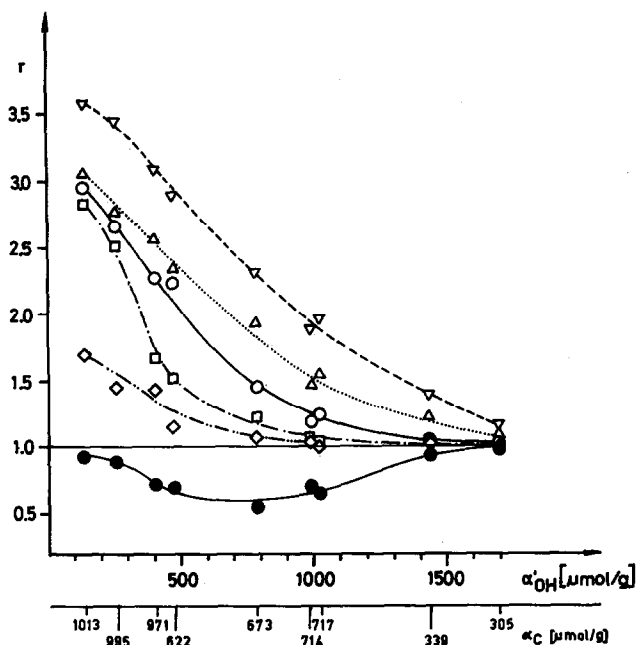


Fig. 6. Relative solute retention with respect to benzene as a function of A_{OH} and A_C . ∇ = Aniline; Δ = phenol; \circ = benzyl alcohol; \square = benzonitrile; \diamond = nitrobenzene; \bullet = butyrophenone. Mobile phase: methanol-water (65:35, w/w).

CONCLUSIONS

Unusual solute retention, peak asymmetry and separation selectivity were correlated with the silanol and organic functional group concentrations of a series of reversed-phase silicas produced by both the usual and high-temperature silylation methods. It was shown that single parameters, such as the concentration of either the organic functional groups or the silanol groups of the silica, are insufficient to account for most of the trends. Compositional and dynamic factors both have to be considered simultaneously if a more complete understanding of the nature of reversed-phase silicas is desired, as subtle interactions between solutes and eluents, such as with crown ethers, might significantly influence the observed chromatographic behaviour.

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