

Influence of alkyl chain length on the stability of n-alkyl-modified reversed phases. 2. Model dissolution study

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Influence of Alkyl Chain Length on the Stability of *n*-Alkyl-Modified Reversed Phases. 2. Model Dissolution Study

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A direct, in situ study of the hydrolysis and dissolution of various *n*-alkyl modified phases was performed with ²⁹Si magic angle spinning NMR spectrometry as a model for stationary phase aging in laboratory practice. With this study, the substantial effect of the ligand length on the dissolution reaction of the alkyl modified phases under aggressive eluent conditions is confirmed. As expected, longer *n*-alkyl ligands gradually show better substrate shielding properties. Above a certain critical ligand length, shielding by longer ligands inhibit the dissolution rate drastically by affecting the hydrolysis and dissolution processes. The type of solvent system used, in liquid chromatography practice or for dissolution studies as reported here, mainly affects the proportions of dissolved silicates in the eluent. On the basis of this in situ dissolution study a model for ligand and substrate hydrolysis and dissolution with the involved reactions is presented.

INTRODUCTION

In the foregoing, accompanying paper it is made clear that one of the most important reasons for instability of stationary phases for reversed-phase high-performance liquid chromatography (RP-HPLC) is concerned with unwanted chemical interactions between the mobile phase and the stationary phase (1). A similar conclusion was drawn in earlier publications from this (2, 3) and other (4) laboratories. Although hydrolysis and dissolution are rather slow processes in LC practice, the RP-HPLC phase deteriorates after a period of intensive use. This is observed by changes in capacity factors, selectivity, and column efficiency.

There are only a few techniques that enable in situ studies of such reversed-phase dissolution. ²⁹Si NMR may provide useful details concerning the molecular structures of species leaving the substrate surface and forming intermediate and final reaction products (5-8). To the best of our knowledge, these studies have been confined to silica gel only, e.g. the substrate part of the stationary phases for RP-HPLC. This prompted us to perform a ²⁹Si NMR study of the dissolution characteristics of several phases for RP-HPLC, investigated in the accompanying paper (1). The stationary phases under study were modified on the same batch of silica substrate using various ligands of increasing *n*-alkyl chain length.

With this study, information on the substantial effect of the ligand alkyl chain length on the various dissolution reactions was obtained. Hence, this paper emphasizes the process of stationary phase deterioration, correlated with the shielding effect of the anchored ligands at the silica surface. The influence of the eluent composition is also considered.

EXPERIMENTAL SECTION

The synthesis and physical characterization of the RP-HPLC phases with varying *n*-alkyl chain length are described in the accompanying paper (1).

Preparation of Solutions. The dissolutions of the reversed phases or the native silica were performed by adding ca. 350 μ L of a 6 M solution of sodium hydroxide in methanol-water (50:50 (v/v)) to approximately 70 mg of stationary phase (this amount was corrected for the ligand content) in a zirconium oxide rotor of the Bruker double air bearing type. In this way a well mixed suspension of Na₂O-SiO₂ with an overall, molar composition of 1:1 was obtained. Similar dissolutions were performed in a 2 M aqueous sodium hydroxide solution in order to obtain an overall, molar composition of 1:3 Na₂O-SiO₂. The well-mixed suspension was introduced into the solid-state NMR spectrometer as quickly as possible.

²⁹Si NMR Measurements. The ²⁹Si NMR spectra were obtained on a Bruker CXP Fourier transform nuclear magnetic

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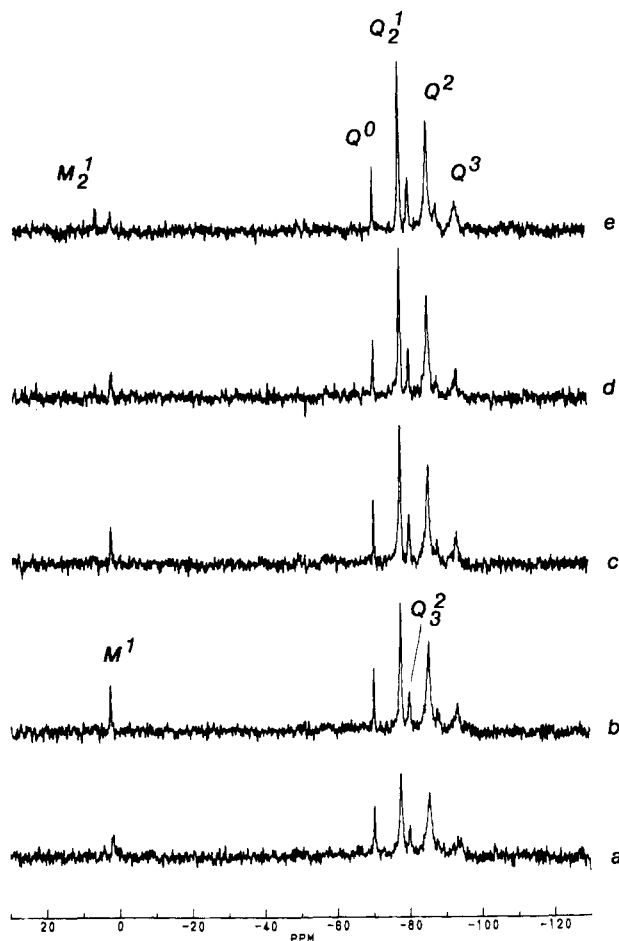


Figure 1. Dissolution of Si-C_4 in an aqueous-methanol-sodium hydroxide solution observed with ^{29}Si MAS NMR after (a) 0.5, (b) 1.5, (c) 3, (d) 6, and (e) 15 h: molar ratio, 1:1 $\text{Na}_2\text{O-SiO}_2$; methanol content, 50% (v/v).

resonance spectrometer at 59.63 MHz. The dissolution studies were performed with magic angle spinning (MAS) NMR to average any chemical shift anisotropies, which might occur in viscous fluids. The well-mixed suspensions were introduced in the zirconium oxide rotor with an outside diameter of 7 mm. The spin frequency used was ca. 1.5 kHz. The spectra were collected at ambient temperature and atmospheric pressure. A 45° flip angle ^{29}Si pulse was applied for excitation. Typically, a series of 30 sequential blocks of 360 accumulated FIDs (free induction decays) with 50 ms acquisition time and 5 s pulse decay were collected in 1K data points each and zero-filled to 8K prior to Fourier transformation. A line broadening of 15 to 25 Hz prior to zero-filling was applied.

RESULTS AND DISCUSSION

The molar $\text{Na}_2\text{O/SiO}_2$ ratios applied for dissolution of chemically bonded phases in aqueous-methanol or plain aqueous systems were selected for practical reasons. The relatively high sodium content ensured hydrolysis and dissolution of the modified silicas within a reasonable time. With the simulated aging experiments 1 L of low pH buffer (pH = 3.0) or high pH buffer (pH = 8.4) was recycled. Thence, possible saturation of the eluent with dissolved ligands and/or silica could occur, reducing the aging effect of the experiments. In RP-HPLC practice, chromatographers commonly use freshly prepared eluents. We will return to this point later.

The reactions involved in the dissolution of the *n*-alkyldimethylsiloxysilane bonded silica substrate were observed with ^{29}Si MAS NMR, by sequential blocks of accumulated acquisitions. Each block represents 30 min of reaction time; see Figure 1. The ^{29}Si NMR spectra of the silica solution exhibited several resonances corresponding to different environments of the ^{29}Si nuclei. These spectra yield also the

Table I. Most Relevant Dissolved Silane/Siloxane Species, Their Functionality, Notation, and Typical ^{29}Si NMR Chemical Shift in the Aqueous-Methanol-Sodium Hydroxide Solution and the Aqueous-Sodium Hydroxide Solution.^a

silane/siloxane species in solution	chemical (spectral) function	topological (network) function	code	typical chemical shift (ppm downfield from TMS)	
				$\text{H}_2\text{O-MeOH}$	H_2O
<i>n</i> -alkyldimethylhydroxysilane	M	0	M^0	+16	+15
<i>n</i> -alkyldimethylsiloxysilane, dimer ^b	M	1	M_2^1	+7	
<i>n</i> -alkyldimethylsiloxysilane	M	1	M^1	+3	
tetrahydroxysiloxane	Q	0	Q^0	-70.4	-71.9
trihydroxysiloxane, dimer ^b	Q	1	Q_2^1	-77.9	-79.9
dihydroxysiloxane, cyclic trimer ^b	Q	2	Q_3^2	-80.3	-81.6
dihydroxysiloxane	Q	2	Q^2	-85.4	-88.4
hydroxysiloxane	Q	3	Q^3	-93.7	-96.9
tetrasiloxysilane	Q	4	Q^4	-106	

^a If not mentioned, the species are part of small oligomers. ^b The subscript refers to the number of particular sites within a dissolved silicate species. In the nomenclature these silicates are also referred to as one species: M_2^1 , 1,2-di-*n*-alkyltetramethyldisiloxane; Q_2^1 , hexahydroxydisiloxane; Q_3^2 , hexahydroxycyclotrisiloxane.

proportions of mono- and tetrafunctional silicon atoms in the solution. The silicon atoms are denoted by M^n ($n = 0, 1$) and Q^n ($n = 0, 1, 2, 3, 4$). This nomenclature was introduced by Engelhardt et al. (6). The chemical shifts of resonance peaks in the ^{29}Si NMR spectra of aqueous-methanol or aqueous-sodium hydroxide silicate solutions are presented in Table I. The ^{29}Si NMR chemical shifts of quaternary siloxanes are in agreement with previous assignments for dissolution/solvation of aqueous silica gel systems (5, 9). The M^0 and M_2^1 ^{29}Si NMR chemical shifts were derived from trimethylethoxysilane and hexamethyldisiloxane, respectively (9). The ^{29}Si NMR chemical shift assignment of the oligomeric *n*-alkyldimethylsiloxysilane M^1 should be considered as preliminary. Shielding by chemical bonding to an oligomeric silicate species in solution could be responsible for a shift of approximately 4 ppm to higher field. This ligand attached silicate species was formed by direct dissolution of oligomeric silicates species from the silica gel.

Silica can be dissolved in highly alkaline media (pH > 11), where the hydroxyl anion is considered to be a catalyst (5, 10). As such, silica dissolves in the form of monomeric tetrahydroxysiloxane, $\text{Si}(\text{OH})_4$ (Q^0). Presumably, formation of monomeric silicate anions in the solution leads to oligomerization of the monomers to hexahydroxydisiloxanes (Q_2^1), hexahydroxycyclotrisiloxanes (Q_3^2), polymeric dihydroxysiloxanes (Q^2), and polymeric hydroxysiloxanes (Q^3). Only recently, chemical exchange between various dissolved silicates (e.g. between Q^0 monomer and Q_2^1 dimer or Q_3^2 trimer) was demonstrated elegantly by Knight et al. (7).

In the present study, ^{29}Si NMR spectra of the dissolution and subsequent reactions of the *n*-butyldimethylsiloxysilane modified silica substrate (Figure 1) revealed a fast dissolution of the reversed-phase material with formation of monomeric tetrahydroxysiloxane followed by oligomerization to polymeric silicate species. The tetrahydroxysiloxane Q^0 level in the

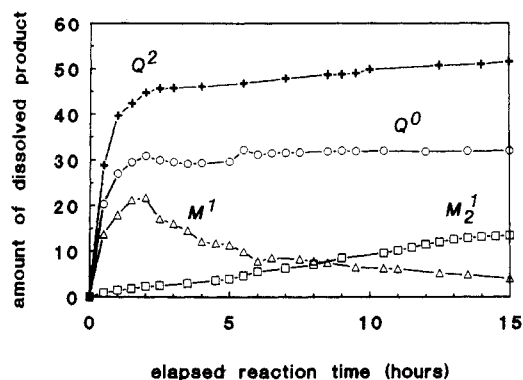
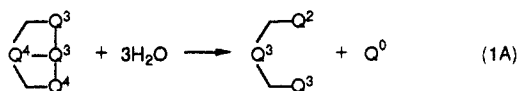


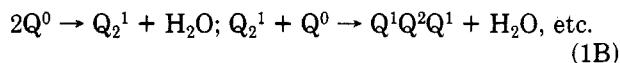
Figure 2. Curves of the relative signal intensities observed with ^{29}Si MAS NMR of several dissolved products from Si-C_4 in the aqueous-methanol-sodium hydroxide solution with elapsed reaction time: molar ratio, 1:1 $\text{Na}_2\text{O-SiO}_2$; methanol content, 50% (v/v).

methanol-water solution seemed to be rather low compared with results of silica dissolution studies published (5, 11). Possibly, the subsequent oligomerization reaction proceeded relatively fast compared with the monomer dissolution under our experimental conditions. Already after half an hour substantial amounts of various oligomers were determined. An equilibrium was reached after approximately 2 h. The ratios of the various dissolved silicates remained almost constant with time, only the signal areas of the oligomers increased slightly.

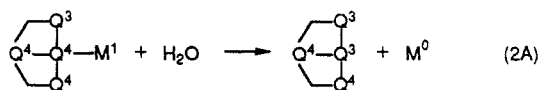
After 1 h a significant amount of *n*-butyldimethylsiloxysilane (M^1), as part of small oligomer species was detected in the solution. After approximately 2 h this started to decrease. It turned out that a secondary product, a di-*n*-butyltetramethylsiloxane dimer (M_2^1), was formed by continued hydrolysis and condensation. The reactions can be summarized in the following scheme (for nomenclature, see Table I): (1A) Dissolution of silica substrate, hydrolysis of siloxane bonds



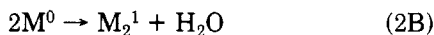
(1B) Oligomerization



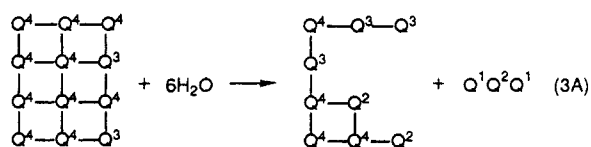
(2A) Hydrolysis of silica to silane bonds



(2B) Dimerization of silane



(3A) Oligomeric dissolution of silica, e.g.



(3B) Oligomeric dissolution of silane-bonded silica, e.g.

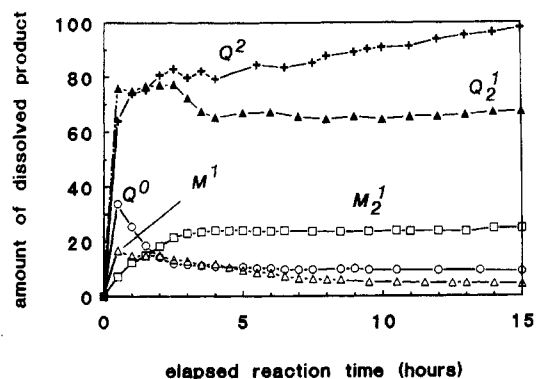
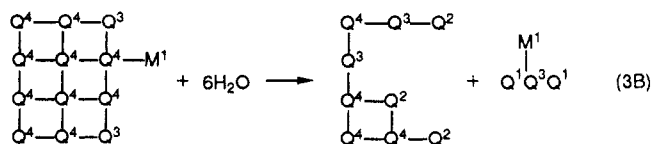


Figure 3. Curves of the relative signal intensities observed with ^{29}Si MAS NMR of several dissolved products from Si-C_1 in the aqueous-methanol-sodium hydroxide solution with elapsed reaction time: molar ratio 1:1 $\text{Na}_2\text{O-SiO}_2$; methanol content, 50% (v/v).

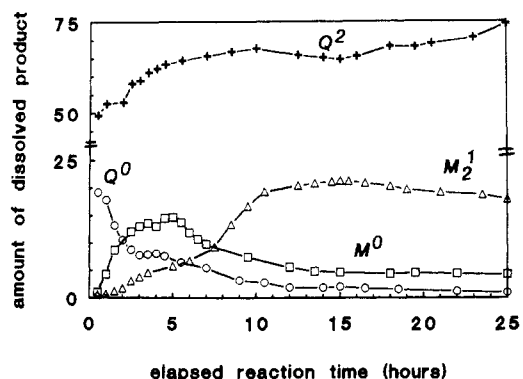


Figure 4. Curves of the relative signal intensities observed with ^{29}Si MAS NMR of several dissolved products from the Si-C_{18} phase in the aqueous-methanol-sodium hydroxide solution with elapsed reaction time: molar ratio, 1:1 $\text{Na}_2\text{O-SiO}_2$; methanol content, 50% (v/v).

Figure 2 depicts curves of the signal intensities of several dissolved products from Si-C_4 in the aqueous-methanol solution with elapsed reaction time.

Very similar spectra as for Si-C_4 were obtained from the dissolution of the trimethylsiloxysilane bonded silica (Si-C_1) in the aqueous-methanol solution under the same conditions as above. In this case, however, both dissolved ligand-silicates M^1 and M_2^1 were formed directly from the start (see Figure 3). An equilibrium between these two dissolved species was attained after about 2 h. Up to *n*-hexyldimethylsiloxysilane modified silica analogous ligand-silicates were observed upon dissolution.

The ^{29}Si NMR spectra following the dissolution of the *n*-octadecyldimethylsiloxysilane bonded phase in the aqueous-methanol solution revealed a rather similar pattern. Figure 4 depicts curves of the signal intensities of several dissolved products with Si-C_{18} in the aqueous-methanol solution with elapsed reaction time. The dissolution rate of tetrahydroxysiloxane monomer was clearly decreased by the longer octadecyl ligands attached to the silica surface.

The dissolution characteristics of the native silica in the aqueous-methanol-sodium hydroxide solution are depicted in Figure 5. The equilibrium was attained rapidly. The proportions of dissolved silicates agreed with those of the short alkyl ligand modified phases, only the amount of dissolved monomer silicates observed was much less. Major concurrent dissolution of small oligomeric silicate species (reaction 1B) probably affected the monomer content by chemical exchange with already dissolved monomeric silicates (7).

Dissolution studies of other *n*-octadecyl modified silicas revealed that the proportions of dissolved silicates depended primarily on the hydrolysis and dissolution rate of tetra-

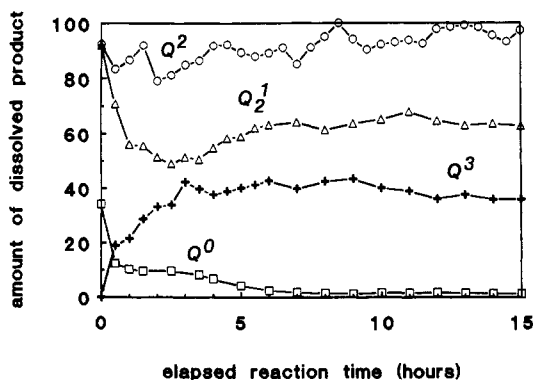


Figure 5. Curves of the relative signal intensities observed with ^{29}Si MAS NMR of several dissolved products from the native silica in the aqueous-methanol-sodium hydroxide solution with elapsed reaction time: molar ratio 1:1 $\text{Na}_2\text{O}-\text{SiO}_2$; methanol content, 50% (v/v).

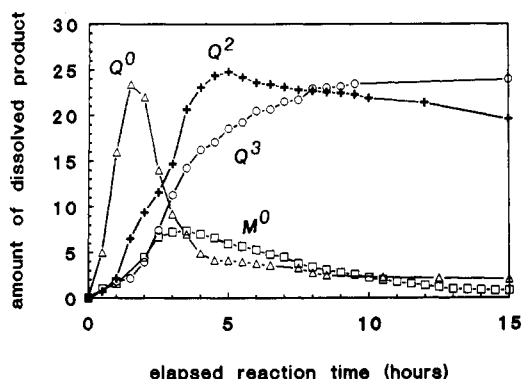


Figure 6. Curves of the relative signal intensities observed with ^{29}Si MAS NMR of several relevant dissolved silicates and ligand attached silicates from $\text{Si}-\text{C}_4$ in the aqueous-sodium hydroxide solution with elapsed reaction time: molar ratio, 1:3 $\text{Na}_2\text{O}-\text{SiO}_2$.

hydroxysiloxanes, Q^0 . Furthermore, the proportions of the oligomeric silicates in particular were affected by the type of solvent used for dissolution studies as is the case with silica substrates (5, 11).

As an example of this sensitivity toward solvents, the course of the dissolution of the *n*-butyldimethylsiloxysilane modified silica in an aqueous, no modifier added, sodium hydroxide solution with a molar composition of 1:3 $\text{Na}_2\text{O}:\text{SiO}_2$ are depicted in Figure 6. Almost equal spectra were collected from the dissolution of $\text{Si}-\text{C}_1$ and $\text{Si}-\text{C}_{12}$ under these conditions. Due to a smaller sodium hydroxide content, the hydrolysis and dissolution of monomeric silicate started more slowly. The smaller oligomerization rate at the start of the experiment allowed a higher content of tetrahydroxysiloxane to be formed in the aqueous solution. Substantial amounts of *n*-alkyldimethylhydroxysilanes were observed with the dissolution in the aqueous buffer solution ($\text{pH} > 12$) of the modified silicas. Condensation of this monomer to dimeric silicate was not detected. Presumably, oligomerization with large silicate oligomers results in less mobile ligands, that are hardly detectable.

Comparison of the different dissolution reactions yields the following. It can be concluded that the apparent detachment of short ligands from the modified silica surface was in fact caused by hydrolysis and dissolution of the underlying substrate silica; see reaction 3B. Thence, we conclude that with advanced monomer dissolution small oligomeric silicate species were concurrently dissolved with monomeric silicates in our aqueous-methanol solvent system.

This concurrent dissociation of oligomeric silicates could be influenced by the open structure of the silica gel studied here. The rather thin pore walls/boundaries could enhance

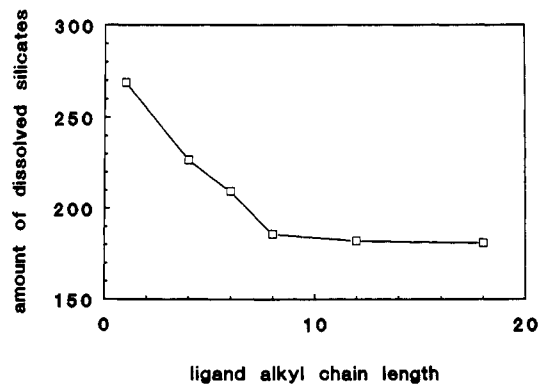


Figure 7. Total amount of dissolved silicates determined by ^{29}Si MAS NMR after 15 h of reaction time for the *n*-alkyl modified phases in an aqueous-methanol-sodium hydroxide solution: molar ratio, 1:1 $\text{Na}_2\text{O}-\text{SiO}_2$; methanol content, 50% (v/v).

dissolution of small silicate pieces.

A different situation prevails for the longer chain modified silicas. Fast oligomerization of the monomeric silicate reduced the amount of monomer and subsequent products of reaction 1B in the solution to a very small value. As a result relatively more polymeric dihydroxysiloxanes, Q^2 , and hydroxysiloxanes, Q^3 , were observed after 15 h of dissolution of silica substrate modified with the octadecyl ligand. Here again, an equilibrium for the dissolved silicates was attained after approximately 2 h.

In fair agreement with all other evidence produced in this study, the amount of dissolved ligand-silicates were relatively small for longer ligands. Furthermore, the removal of longer ligands from the silica surface occurred mainly by direct hydrolysis to form *n*-octadecyldimethylhydroxysilanes, M^0 . Subsequent condensation with other dissolved monomeric silicates resulted in di-*n*-octadecyltetramethyldisiloxane dimers, M_2^1 , reaction 2B. Presumably, steric hindrance and boundaries caused by van der Waals interactions between neighboring ligands inhibited direct dissolution of small ligand-silicate oligomeric species from the silica surface. It seemed that dissolution of oligomeric silicate species was reduced likewise. Analogous dissolution behavior was observed for the $\text{Si}-\text{C}_8$ and $\text{Si}-\text{C}_{12}$ phases.

The total amount of dissolved silicate species determined after $\text{Si}-\text{C}_1$, $\text{Si}-\text{C}_4$, and $\text{Si}-\text{C}_6$ dissolution in the aqueous-methanol-sodium hydroxide solution was significantly higher than after $\text{Si}-\text{C}_8$, $\text{Si}-\text{C}_{12}$, and $\text{Si}-\text{C}_{18}$ dissolution with a corresponding amount of stationary phase under identical conditions; see Figure 7. The *n*-octyldimethylsiloxysilane phase obviously possessed a kind of critical ligand chain length for dissolution of the modified silicas.

The translation of the dissolution studies described here to the aging of RP-HPLC stationary phases can be made as follows. The model dissolution studies were performed as a batch process in limited volume rotors (350 μL) with rather high pH solvents ($\text{pH} > 12$). The relatively high sodium content ensured hydrolysis and dissolution of the modified silicas within a reasonable time. In this small volume under the experimental conditions, saturation of the solvent may well affect the further dissolution of the reversed-phase materials. A comparison of dissolution and stationary phase hydrolysis in daily chromatography practice is subject to certain restrictions. The oligomerization reactions observed in the sodium hydroxide solution may be promoted as a consequence of a high concentration of the primary dissolution products. Probably, when freshly prepared eluents are used, only hydrolysis and dissolution of ligands and silica without subsequent oligomerization will be the main causes of stationary phase degradation. Thence, the primary dissolution reactions observed with ^{29}Si NMR spectroscopy here reflect

the main course of the dissolution process that occurs under RP-HPLC conditions in practice. Factors affecting this process should be considered for stationary phase hydrolysis and dissolution.

CONCLUSIONS

Two fundamentally different ligand dissolution processes are observed in an aqueous-methanol solution. Short alkyl ligand modified silica gels degrade by concurrent dissolution of monomeric tetrahydroxysiloxane (reaction 1A) and small oligomeric silicate particles of subcolloidal level (<1-3 nm) (5). The process of oligomer dissolution (reactions 3A and 3B) enhances the degradation rate of short alkyl modified silicas drastically.

Longer alkyl ligand modified silicas degrade mainly by monomeric dissolution of silica (reaction 1A). Surface attached ligands are hydrolyzed and dissolved as *n*-alkyldimethylhydroxysilanes (reaction 2A).

The use of water as a solvent promotes monomeric dissolution, also with short alkyl ligand modified silicas.

The *n*-octyl bonded phase exhibits the critical ligand alkyl chain length upon modification of the silica substrate used in this study, with respect to direct oligomer dissolution in aqueous-methanol solvents.

For short alkyl ligand bonded phases multidentate surface attachment will not prevent dissolution of the ligands, due to oligomer dissolution. Polymer coated stationary phases or neighbor attached silanes, cross-linked across the silica surface may prevent severe dissolution of the short ligands by oligomer dissolution. Specific surface shielding groups (e.g. pre- or end-capping with trimethylsiloxysilanes) may contribute also

to prevent degradation of the stationary phases. Longer *n*-alkyl ligands with large enough surface concentration should be preferred with aggressive eluents. Preliminary experiments involving dissolution of bi- and trifunctionally derivatized silicas ("polymeric") indicate that product ratios are formed, considerably different from those of the monofunctional phases.

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Prediction of Retention Times in Serially Linked Open-Tubular Gas Chromatographic Columns and Optimization of Column Lengths

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The serial gas chromatographic theory, first advanced and then further developed by Purnell and Williams, is used to optimize the analysis of a nine-component phenol mixture by use of linked capillary columns. The capacity factors of sample components with the system serially coupled in either mode, column A/column B or column B/column A, and of different relative length, are shown to agree essentially exactly with those predicted by theory. The window analysis procedure devised by Laub and Purnell is then used to calculate the relative and overall length of the columns required to achieve base-line resolution. The experimental chromatograms are shown to correspond precisely to prediction. When the methodology is applied generally, it is shown that the requisite data can be determined easily and rapidly and the subsequent calculations can be carried out via an equally simple computer program. The consequent techniques and procedures should help the development of serial-coupled open-tubular column chromatography (SCOTCH).

INTRODUCTION

Early interest in the analytical use of serially linked gas chromatographic columns led to the observation that reten-

tions of mixture components were not simple averages of the values for the individual columns and, further, depended also on the column sequence. This work was reviewed in detail in the pioneering study of Hildebrand and Reilley (1) who, in 1965, developed an approximate theory adequate to explain the above effects, although it failed quantitatively in most cases of application. Interest in the topic then waned, except for the brief studies by Buys and Smuts (2) and Krupcik, Guiochon, and Schmitter (3). However, the potential of linked capillaries attracted fresh interest (4, 5) in the early 1980s; unfortunately, the inadequate theoretical basis available led to failure to account for retention variation, and therefore column optimization for particular analyses also failed.

In 1984, Purnell and Williams (6) returned to the theoretical problem and, in a series of subsequent papers (7-12), generated the general theory and consequent optimization procedure for serial-column analyses. They showed, using packed columns, both that the theory was valid and that simple procedures could be devised to permit the accurate prediction of retentions with serial columns. In addition, they showed how the window diagram procedure devised by Laub and Purnell (13-16) could be used to evaluate very precisely the relative and total column lengths required to provide optimized separations.