SYNTHESIS OF THREE ALKYLDIHYDROCHLOROSILANES AND THEIR APPLICATION IN STUDIES OF STERIC FACTORS IN THE SURFACE DEACTIVATION OF POROUS SILICA

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SUMMARY

The synthesis and bonding to silica of ethyl-, octyl-, and octadecyldihydrochlorosilane are reported. These silanes are shown to react to a greater extent with surface hydroxyls than analogous alkyldimethylchlorosilanes, and this results in chromatographic stationary phases with reduced residual silanol activity.

INTRODUCTION

Since workers began to bond alkylsilyl groups to the surface of porous silica the understanding of the structure of the solvated bonded phase and its impact on mechanisms of separations in reversed-phase liquid chromatography has grown in detail[1]. These stationary phases are now described as pseudo liquids[2-4], which are mixtures of the bonded moieties and the various mobile phase components which partition themselves into the stationary phase to a degree controlled by their concentrations in the bulk mobile phase and their reversed-phase solvent strengths[5-7]. The selectivities of these bonded phases arise from solvation interactions between the solutes and the various components of the stationary phases, namely the bonded moieties[8,9], the imbibed solvent molecules[6,7], and the residual surface hydroxyls that remain after the bonding process[10-12]. In recent work, it has been shown that various solutes find their most favorable interactions in different regions of the stationary phase, and it has been proposed that a polarity excursion is experienced by the sorbed solute molecule that is greatest in the near-surface region of silanols and adsorbed water reaches a minimum near the center region of the stationary phase, and increases to that of the bulk mobile phase as the solute molecule moves up through the solvated layer from the silica surface[13]. Thus, the apparent polarity of bonded phases is both a function of the alkyl group(s) of the bonding silane and the extent to which the bonding has proceeded[12-16]. Researchers have long studied the role of residual surface hydroxyls in yielding the particular properties of silica-based adsorbents, and the question how bonded phases would behave if the activity of these residual sites was completely removed is still unanswered[12].

Two families of alkylsilanes have traditionally been used to modify the surface of porous silica. They have been called monomeric and polymeric modifiers, respec-

tively. Each class has advantages and, depending on the application of the adsorbent in question, one type or the other can be the modifier of choice[15]. Monomeric modifiers of the general formula $R(CH_3)_2SiX$ (where X is some easily hydrolyzed group) have the advantages of greater reproducibility, reduced activity, and conformation to the original topography of the silica, because the bonding molecule deactivates surface sites without the possibility of creating new ones[15,17]. Polymeric modifiers of the general formula $RSiX_3$ have the advantages of higher carbon load, shorter reaction time, and increased stability towards hydrolysis[15,18]. One of the causes of the variable features of polymeric phases is the tendency of these reagents to react with trace amounts of water present in the solvent or extracted from the silica and then to polymerize in solution before bonding to the surface hydroxyls in ways that may or may not conform to the original surface[18,19]. It is for this reason that researchers investigating mechanisms have preferred monomeric modifiers. The goal of this research has been to develop a new family of surface modifiers that would combine the reproducibility and reduced polarity attainable with monomeric modifiers with the stability and higher carbon load attainable with polymeric modifiers.

This paper describes the synthesis of a family of surface modifiers of the general structure RH_2SiCl that may afford higher carbon load and yet conform to the original surface structure of the substrate. This new family of surface modifiers reacts with surface hydroxyls as monomers and leads to higher surface coverages because of the reduced size of the bonding silane which has had the bulky methyl groups replaced with hydrogens. After bonding, the silylhydrides can be oxidized to Si–OH groups, possibly allowing these materials to take on the properties of and serve as models for polymeric systems. The bonding of these new modifiers to porous silica is described, along with spectroscopic and chromatographic characterization of the resulting materials. Also, the properties of these new adsorbents are compared to those of the same type of silica that has reacted with the analogous alkyldimethyl-chlorosilanes.

EXPERIMENTAL

Reagents
        Methanol, toluene, hexane (isomeric mixture), benzene, and mercuric chloride, all analytical-reagent grade, were obtained from Fisher Scientific (Fair Lawn, NJ, U.S.A.); ethyldimethylchlorosilane, ethyltrichlorosilane, octyldimethylchlorosilane, octadecyldimethylchlorosilane, and dichlorosilane from Petrarch (Bristol, PA, U.S.A.); 1-chlorooctadecane, trimethylchlorosilane, dibromomethane, glyme, phenol, phenethyl alcohol, 3-phenyl-1-propanol, 4-phenyl-1-butanol, 5-phenyl-1-pentanol, and lithium aluminum hydride from Aldrich (Milwaukee, WI, U.S.A.); Grignard-grade magnesium turnings, acetophenone, 30% hydrogen peroxide, methylbenzoate, anisole, and aniline from Mallinckrodt (Paris, KY, U.S.A.); anhydrous diethyl ether and benzylamine from J. T. Baker (Phillipsburg, NJ, U.S.A.); 1-chlorooctane from Eastman (Rochester, NY, U.S.A.); and dibutyltin diacetate from Alpha Products (Danvers, MA, U.S.A.). All solvents brought into contact with silica particles were filtered using $0.45-\mu m$ membrane filters, obtained from Millipore (Bedford, MA, U.S.A.). Glyme was distilled from lithium aluminum hydride before use, and distilled water was redistilled from a solution of potassium permanganate and potassium hydroxide. All other chemicals were used without further purification.

Synthesis of octyldihydrochlorosilane (ODHCS) and octadecyldihydrochlorosilane (ODDHCS)

Octyl magnesium chloride or octadecyl magnesium chloride, prepared from the corresponding alkyl chloride, was added while refluxing to a 1.3-fold excess of dichlorosilane in diethyl ether. The resultant solution was decanted and fractionally distilled at reduced pressure through a 15-cm Vigreux column: ODHCS distilled at 60.5°C and 4 Torr; ODDHCS distilled at 142°C and 0.3 Torr. The yield of purified product in both instances was about 40%, based on the initial amount of the alkyl chloride. Both structures were verified by transmission infrared spectrophotometry with a Perkin-Elmer (Norwalk, CT, U.S.A.) Model 983 IR spectrophotometer, by proton NMR spectrometry with a Varian (Sunnyvale, CA, U.S.A.) Model T-60 NMR spectrometer, and by mass spectrometry with a Hewlett-Packard (Palo Alto, CA, U.S.A.) Model 5990A gas chromatograph–mass spectrometer.

Synthesis of ethyldihydrochlorosilane (EDHCS)

The method used was similar to that used by Anderson and Hendifar[20] in the synthesis of heptyldihydrochlorosilane. Ethyltrichlorosilane was reduced by addition to a slurry of lithium aluminum hydride in glyme. The resulting ethylsilane (b.p. -59°C) was condensed and dissolved in glyme, cooled by a dry ice–methanol slurry. An equimolar amount of mercuric chloride was added to the cooled solution over the course of 3 h. The formation of metallic mercury indicated the progress of the reaction. The mixture was then heated over a period of 3 h until the reflux temperature reached 40°C. The product was recovered by fractional distillation. The yield of purified product was 55%, based on the initial amount of ethyltrichlorosilane. The identity of EDHCS (b.p.$_{760}$ 43°C) was confirmed by gas chromatography–mass spectrometry.

Silica modification

The silica used in this study was obtained from Lochmuller (Duke University, Durham, NC, U.S.A.) and is part of a single batch (Id. No. RR-129-7A), donated by Whatman Chemical Separation (Clifton, NJ, U.S.A.) that has been used by Lochmuller and others in surface modification studies. This silica had been acid-washed and was used here without further treatment. The manufacturer reports a mean particle size of 7.53 μm, an average pore diameter of 96 Å, and a nitrogen BET surface area of 323 m^2/g. The bonding of all silica samples was accomplished by refluxing the sample in a 10% (v/v) solution of the silylating agent in toluene, in a volume calculated to contain at least a five-fold excess of the silylating agent for the number of surface hydroxyls present (based on the weight of the sample, the reported surface area, and the assumption of 4–5 silanols per nm^2). The silica samples were refluxed under dry nitrogen purge for the indicated amount of time, which varied from 2 to 72 h. Each sample was then filtered through a 5-μm membrane filter and washed at least ten times with 30 ml of fresh toluene and then ten times with 30 ml of methanol. The samples were dried overnight at 120°C under reduced pressure (*ca.* 0.1 Torr). The percentage carbon atoms of each sample was determined by combustion analysis, using a Perkin-Elmer Model 240C elemental analyzer.

Spectroscopic characterization

Transmission infrared spectra of bonded silicas were obtained as mulls with carbon tetrachloride in capillary cells with sodium chloride windows. The cross-polarization magic-angle spinning (CPMAS) ^{29}Si NMR spectrum of silica bonded with ODDHCS was graciously provided by the Regional NMR Facility (Boulder, CO, U.S.A.).

Chromatographic characterization

Samples of bonded silica were packed as a density-balanced slurry of dibromomethane and methanol or of dibromomethane and hexane. Approximately 0.3 g of silica were slurried in 4.5 ml of density-balanced solvent and sonicated for 10 min. The slurry was then added to a 250 × 4.6 mm stainless-steel packing bomb, coupled to a 100 × 2.1 mm stainless-steel column with a 2-μm stainless-steel frit in the outlet end. The packing bomb was then connected to a pneumatically driven pump, and methanol or hexane was pumped for 10 min at 6000 p.s.i. Chromatographic experiments were carried out with an IBM Instruments (Danbury, CT, U.S.A.) Model 9533 ternary solvent gradient liquid chromatograph. The elution of UV-absorbing solutes was monitored with an IBM Instruments Model 9522 fixed-wavelength UV absorbance detector at 254 nm. The elution of non-absorbing solutes was monitored with a Micromeritics (Norcross, GA, U.S.A.) Model 771 refractive-index detector. The retention times of solutes were measured with a Linear Instruments (Irvine, CA, U.S.A.) Model 261/MM strip-chart recorder. Flow-rates were measured by noting the time required to collect a given volume in a precision buret. Extra-column volumes were measured by replacing the column with a zero-dead-volume union. Maximum void volumes were measured as the elution volume of pentane or heptane with hexane as the mobile phase. Capacity factors were calculated using the maximum void volume thus measured and corrected for extra-column volume.

RESULTS AND DISCUSSION

The synthesis of several alkyldihydrochlorosilanes, including methyl-[21], ethyl-[22], propyl-, butyl-[23], and heptyl-[20], by various methods has been reported, but these compounds are not widely used and are therefore not commercially available. The synthetic methods used fall into two classes: (1) the chlorination of the alkylsilane with[21] or without[20] a catalyst, and (2) the disproportionation of the alkyldichlorosilane with the help of some catalysts. As catalysts aluminium chloride[22] or some mild organic base such as a nitrile[23] have usually been used. The synthetic method used for ODHCS and ODDHCS, both previously unreported compounds, was chosen because of the ready availability of dichlorosilane, and because the most likely impurity to be produced in each case was the disubstituted alkylsilane, which would be easy to separate from the desired product due to the large difference in boiling point. This method was not used for EDHCS because of the difficulty of separating it from dichlorosilane.

Many researchers have bonded $R(CH_3)_2Si-$ groups to silica with the result that the number of groups bonded was always less than the calculated number of silanols present, the calculation being based on the surface area, as measured by the nitrogen BET isotherm method and by assuming 4–5 silanols per nm^2. The best
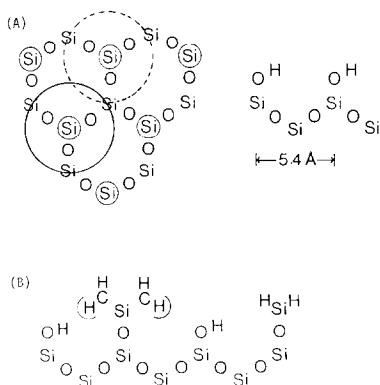
Fig. 1. (A) Two-dimensional schematic representation of an idealized silica surface, showing the approximate size of bonded trimethylsilyl groups and the maximum distance between neighboring silanols. Bonded trimethylsilyl groups are represented by large solid circle. The large broken circle represents the location of a trimethylsilyl group reacting with a neighboring silanol. Ⓢ shows the original location of silanol. (B) Two-dimensional schematic representation of an idealized silica surface, showing the approximate size of bonded silanes $R(CH_3)_2Si-$ vs. RH_2Si-.

coverage is attained with trimethylchlorosilane (TMCS), which implies that the limitation is steric hindrance. Calculation of the surface required for each TMCS group, based on its density or the density of tetramethylsilane, yields a value of about 35 $Å^2$, in agreement with the usually reported values of coverage by TMCS which lie between 60 and 70% of the predicted number of silanols present[12,24,25]. It was assumed that, if the size of the groups filling the valencies of the bonding silicon atom could be reduced, the coverage attainable by such a molecule would increase relative to its predecessors.

Fig. 1A is a two-dimensional view of silica, approximately to scale, where the fourth bond to each silicon atom is directed into or out of the page. The large, solid circle shows the projected surface area (35 $Å^2$) occupied by a bound trimethylsilyl
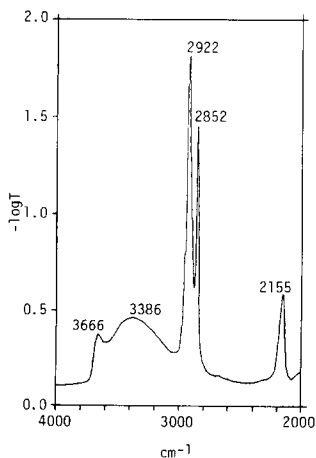

Fig. 2. Transmission IR spectrum of ODDHS-bonded silica after six months' exposure to air.

group. The distance between neighboring silanol groups of 5.4 Å is certainly an upper limit, but, as can be seen in the diagram, the bound $R(CH_3)_2Si-$ group is large enough to hinder sterically the bonding of another silane (represented by the broken circle) to either of the neighboring silanols. Shown in Fig. 1B is the increased freedom obtained by replacing the bulky methyl groups with hydrogens. In order to investigate this idea, the three new modifiers were applied to the surface of silica by the method outlined. To verify that the potentially unstable Si–H groups had remained intact during the bonding process, the IR spectrum of each sample was taken between 4000 and 2000 cm^{-1}, and the intensity of the Si–H stretch at 2155 cm^{-1} was compared to that of the C–H stretches between 3000 and 2750 cm^{-1}. For fresh samples, the relative intensities of these two bands were within the precision of measurement of the expected value, assuming that no change in absorptivity occurred upon bonding to the surface.

Fig. 2 is the IR spectrum from 4000 to 2000 cm^{-1} of an octadecyldihydrosilyl (ODDHS)-bonded silica which had been exposed to air for six months. The integrated area of the absorption peak at 2155 cm^{-1} due to the Si–H stretching vibration is approximately 22% of the combined area of the peaks at 2920 and 2850 cm^{-1} due to the C–H stretching vibrations. The area of the peak due to the Si–H stretches in a neat sample of ODDHCS is 32% of the area of the C–H stretches. Assuming that the absorptivities of the respective vibrations have not changed, this would indicate that 31% of the Si–H groups originally present had been oxidized to Si–OH groups.

Fig. 3 is the CPMAS ^{29}Si NMR spectrum of the same sample. The peaks at -15 and -30 ppm have tentatively been assigned to the signals arising from $-OSiH_2R$ and $-OSiHOHR$ groups, respectively. If it can be assumed that the area measurements of these peaks are quantitative, this spectrum indicates that 29% of the Si–H groups originally present had been oxidized, which is in good agreement with the IR results. The fact that this sample was exposed to air for six months illustrates the stability of these bound Si–H moieties. It is just this stability which allowed us to characterize these bonded phases in their reduced form. IR spectra of
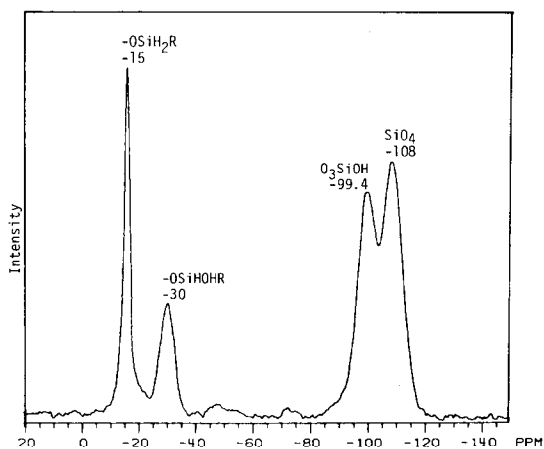

Fig. 3. CPMAS ^{29}Si NMR spectrum of ODDHS-bonded silica after six months' exposure to air.
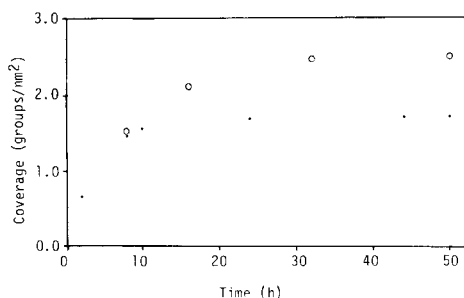
Fig. 4. Plot of coverage of silica by octadecylchlorosilanes *vs.* reaction time. (○) –ODDHCS; (●) – ODDMCS.

ODDHS-bonded silica samples, removed from the column after the completion of chromatographic experiments, indicated that most of the Si–H groups were still present, although no rigorous quantitation was attempted.

The first comparison to be made between $R(CH_3)_2SiCl$ and RH_2SiCl modifiers was the extent to which they could be bonded to a given silica surface. Each coverage is reported as groups per $R(CH_3)_2SiCl$ and is calculated from the percentage carbon atoms obtained from combustion analysis. The manufacturer's reported surface of 323 m²/g was used in the following formula:

$$\frac{X_0(12.01/n_0)N}{\{1 \;-\; [X_0(12.01/n_0)\,(MW \;-\; 1.008)]\}323 \cdot 10^{10}}$$

in which X_0 is the measured mass fraction of carbon, n_0 is the number of carbons in each bonded group, N is Avagodro's number, and MW is the calculated formula weight of the alkylsilyl radical.

Fig. 4 shows the coverage of octadecyldimethylchlorosilane (ODDMCS) and ODDHCS *vs.* reaction time under the conditions described. As is indicated by the plot, the extent of bonding by each type of modifier seems to be roughly equivalent at short reaction times, but the reaction between silica and ODDMCS levels off faster
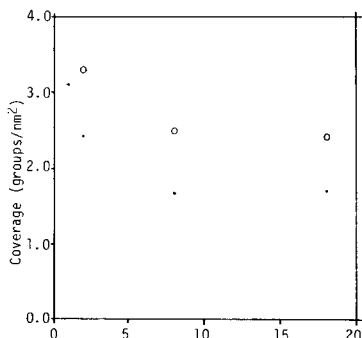

Fig. 5. Plot of maximum coverage attained by alkylchlorosilanes *vs.* chain length. (○) –RH_2SiCl; (●) $R(CH_3)_2SiCl$.

TABLE I

INCREASE IN SURFACE COVERAGE AVAILABLE BY REPLACING PENDANT METHYL GROUPS WITH HYDROGENS

H = Maximum coverage attained by RH_2SiCl; M = maximum coverage attained by $R(CH_3)_2SiCl$.

R	H–M (groups per nm²)
Ethyl	0.87
Octyl	0.85
Octadecyl	0.71

than the reaction between ODDHCS and silica after about 10 h. The latter does not reach a plateau until at least 32 h of reaction time. In order to compare the full extent to which each modifier could be bonded, reaction times of at least 32 h were always employed. It is also worth noting that the shape of the kinetic curves shown did not change if the sample was periodically removed and washed, and the reaction was continued after the addition of fresh reagent.

Fig. 5 shows the maximum coverage attainable with chlorosilanes as a function of chain length of the alkyl group R– for the two types of modifiers, $R(CH_3)_2SiCl$ and RH_2SiCl. In all cases, the RH_2SiCl modifier yielded higher coverages than the dimethyl analogue. However, it is interesting to note that the two curves generated by the respective classes of modifiers seem to be parallel, indicating that, regardless of the length of the hydrocarbon chain filling the fourth valency of the bonding silicon atom, the increase in coverage available by replacing the two methyl groups with hydrogens is constant. Table I is a list of the differences in coverages given by each pair of the different types of modifiers of equal chain length. Although methyldihydrochlorosilane has not yet been successfully synthesized and bonded to silica in our laboratory, the above plot indicates that it should yield a coverage around 4 groups per nm². Experiments are currently underway in our laboratory to test this hypothesis and will be reported in the near future.

To determine which type of modifier would leave silica with the least amount of residual activity, a chromatographic comparison was made between silica samples that had been reacted with either ODHCS or octyldimethylchlorosilane (ODMCS) for 50 h so that in each case maximum coverage had been reached. This coverage was 2.53 groups per nm² for ODHCS and 1.68 groups per nm² in the case of ODMCS. Each sample of bonded silica was packed into stainless-steel columns, as described, using hexane as the packing solvent and subsequently as the mobile phase.

TABLE II

RETENTION OF SOLUTES USING HEXANE AS MOBILE PHASE

Silica modifier	Groups per nm²	Capacity factor, k'		
		Anisole	Methylbenzoate	Acetophenone
Octyldihydrochlorosilane	2.53	1.6	6.3	19
Octyldimethylchlorosilane	1.68	2.4	12	34

Hexane was chosen as the mobile phase because of its structural similarity with the bonded hydrocarbon chains. Thus, any retention observed could be directly attributed to residual silanol activity. The particular solutes chosen were small molecules that could be conveniently detected by UV absorption at 254 nm, had functional groups that could interact with silanols to varying extents, and would be eluted in reasonable time. Anisole, methylbenzoate, and acetophenone fit this description. The capacity factors for these solutes are reported in Table II. The retention of all three solutes by silica, modified with ODMCS, is roughly twice that of silica modified with ODHCS. The ability of ODHCS to deactivate silica to a greater extent than ODMCS indicates promise for this new family of surface modifiers.

In order to investigate the extent to which the deactivation of silica by alkyldimethylchlorosilanes can be attributed to steric exclusion of solutes from existing silanols by the pendant methyl groups, a comparison was made between silica samples that had been modified by either ODDHCS or ODDMCS in such a way that the coverage by each modifier was approximately the same. This was accomplished by stopping the bonding process early (8 h for ODDHCS and 10 h for ODDMCS). The coverage on the ODDHS-bonded silica was 1.53 groups per nm^2 and the coverage on the octadecyldimethylsilyl (ODDMS)-bonded silica was 1.59 groups per nm^2. The retention of methoxybenzene and methyl benzoate in a mobile phase of hexane was used to measure the residual silanol activity. The resulting capacity factors are also listed in Table III. The capacity factors in Table III cannot be compared with those in Table II, because the hexane used for the former was drier. However, the comparisons within each table are valid, since the same batch of hexane was used throughout each set of experiments. The retention of both solutes by the ODDHS-bonded silica was roughly twice that of the ODDMS-bonded silica. This shows that even though essentially the same number of silanols was present after bonding, those next to a silicon atom with pendant hydrogens instead of methyl groups were much more available for adsorption by a solute or perhaps for further reaction with a silylating reagent.

It was possible to investigate the role of residual silanols in reversed-phase liquid chromatography in a novel manner, using the previously mentioned pair of octadecylsilyl-bonded columns, because both adsorbents contained approximately the same carbon load (14.41% C for ODDHS-bonded silica and 16.21% C for ODDMS-bonded silica) and very close to the same number of bound octadecyl chains per unit area, but the residual activity of the remaining silanols was very different. The retention of a variety of solutes by both bonded silicas was measured using methanol–water (40:60, v/v) as mobile phase. The solutes were chosen to represent

TABLE III

RETENTION OF SOLUTES USING HEXANE AS MOBILE PHASE

Surface modifier	Groups per nm^2	Capacity factor, k'	
		Anisole	Methylbenzoate
Octadecyldihydrochlorosilane	1.53	8.5	49
Octadecyldimethylchlorosilane	1.59	4.1	21

TABLE IV

COMPARISON OF RETENTION OF SOLUTES USING METHANOL–WATER (40:60) AS MOBILE PHASE

Solute	Capacity factor, k'		Ratio k'_2/k'_1
	ODDHS-bonded silica (k'_1)	ODDMS-bonden silica (k'_2)	
Analine	2.80	2.36	0.84
Benzylamine	5.48	5.39	0.98
Phenol	2.66	2.63	1.01
Benzyl alcohol	2.86	2.88	1.01
Benzaldehyde	5.05	5.15	1.02
Phenethylalcohol	4.76	5.12	1.08
3-Phenyl-1-propanol	9.72	10.74	1.10
4-Phenyl-1-butanol	20.0	22.57	1.13
Benzene	9.61	12.21	1.27
Toluene	22.5	30.3	1.35
Ethylbenzene	48.3	69.0	1.43

a broad range of polarities and functional groups to investigate the range of interactions available with the solvated bonded phase. A phenyl group was also included in each solute for convenient and sensitive detection by UV absorption at 254 nm. The results are shown in Table IV along with the ratios obtained by dividing the capacity factor of each solute in the ODDMS column by the capacity factor of the same solute in the ODDHS column. In order to facilitate the interpretation of the results, the solutes in Table IV can be divided into three categories. Solutes which were more retained by the ODDHS column are basic solutes, solutes about equally retained by both stationary phases are hydrogen-bonding solutes of intermediate polarity, and solutes which were markedly more retained by the ODDMS-bonded silica are the solutes of lowest polarity.

These results can be explained by considering the polarity profile proposed to exist in bonded phases when they are used as reversed-phase sorbents with mixed solvents as the mobile phases[13]. It must be realized that the retention of each solute will be influenced most by changes in the region of the stationary phase where its interactions are energetically most favorable. As observed, solutes retained mostly in the upper regions of the stationary phase, such as the alcohols, should experience little difference between the two stationary phases. Also as observed, solutes interacting with the highest energy in the near-surface region of the stationary phase, such as the basic solutes, should experience a difference between the two stationary phases, reflecting the greater polarity of the ODDHS-bonded silica. Low-polarity solutes, such as the alkylbenzenes, interact most energetically with the central region of the stationary phase, where the polarity is a minimum. The decreased retention of these solutes by the ODDHS-bonded silica indicates that the absence of methyl groups on the bonding silicon atom or in the near-surface region allows silanol groups on the surface to have a greater influence on the polarity of the central region of the stationary phase. Thus, residual silanols serve as high-energy adsorption sites for basic solutes and affect the retention of other solutes by influencing the polarity of other

regions in the stationary phase through hydrogen-bonding interactions with the polar components of mixed mobile phases.

Bonded phases of the type described in this paper would not be of practical use if it were difficult to oxidize the bound Si–H functionalities selectively. If they instead oxidized slowly with use, they would show transient chromatographic characteristics. Much has been written about the use of silyl hydrides as selective reducing agents for organic compounds. Dibutyltin diacetate is a commonly used catalyst for this purpose[26]. By refluxing silica modified with ODDHCS in a solution of dibutyltin diacetate and hydrogen peroxide in methanol for a few hours, 90% of the Si–H groups originally present were oxidized (judging from the intensity of the IR band at 2155 cm^{-1} relative to bands near 3000 cm^{-1}). This is a promising result. Silicon hydrides also readily add across C–C double bonds[27]. This implies that compounds with two double bonds might be used to cross-link neighboring Si–H groups. Experiments designed to oxidize bound silyl hydrides with the intent of cross-linking the newly oxidized surface sites in order to further alter the activity of the surface and to stablize it toward hydrolysis are underway and will soon be reported.

CONCLUSIONS

A group of new alkylchlorosilanes has been synthesized and successfully bound to the surface of silica. It has been shown that alkyldihydrochlorosilanes can be bound in a monomeric fashion to silica and that replacing bulky methyl groups on the bonding silicon atom with hydrogens reduces the steric hindrance of the bonding group and leads to higher surface coverage. It has also been shown that part of the surface deactivitation of silica by alkyldimethylchlorosilanes is due to steric factors. Finally, there is good evidence that surface-bound silyl hydrides can be selectively oxidized for future *in situ* cross-linking of neighboring groups.

ACKNOWLEDGEMENTS

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