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## CHARACTERIZATION OF SILANOL REACTIVITY AND ACIDITY ON OCTADECYL-BONDED CHROMATOGRAPHIC SUPPORTS BY $^{29}\text{Si}$ SOLID-STATE NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND SURFACE TITRATION

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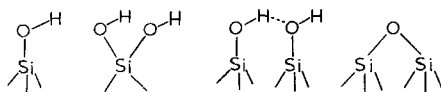
### SUMMARY

Surface analysis and chromatographic data are used to examine the structure of surface groups in a reversed-phase chromatographic environment involving an octadecyl-derivatized silica substrate. The support is characterized by  $^{29}\text{Si}$  solid-state nuclear magnetic resonance spectroscopy and surface titration, and results are compared to other spectroscopic methods for the quantitation of surface species. Quantitative nuclear magnetic resonance data permits examination of the number and reactivity of single versus geminal hydroxyl sites as a function of octadecyldimethylsilyl coverage. It is postulated that an acidic, reactive subset of surface silanols exists that includes a large proportion of the geminal silanol sites, and a subset of the single silanol sites including hydrogen-bonded species such as the vicinal silanols. Knowledge of surface structure helps to explain various types of chromatographic behavior including the inaccessibility of some surface region silanols at moderate silane coverages, the partition-like behavior of octadecyl substrates, and the pH-dependent retention of non-polar solutes in reversed-phase chromatography.

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### INTRODUCTION

The nature of surface sites on silica has been extensively studied revealing structurally distinct surface groups including lone (isolated single), geminal, and vicinal silanols, and siloxanes (shown from left to right).



Both lone and vicinal silanols are included in the category of single silanols, *i.e.* one

covalently bound hydroxyl group per silicon atom. Within these various classes of surface silanol species, there appears to be at least one subset of active sites which account for the primary reactive and acidic properties of the silica. It has long been the aim of various investigators to determine the chemical structure and concentration of these active sites.

Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful technique for elucidating the structure of amorphous solids such as silica, because it can potentially distinguish subtle differences in chemical functionality. The focus of previous cross polarization (CP), magic-angle spinning (MAS)  $^{29}\text{Si}$  NMR experiments involving silica has been the spectral assignment and quantitation of surface species<sup>1,2</sup> as related to surface geometry and reactivity<sup>3,4</sup>. It has been demonstrated that NMR can be used to distinguish and quantify single and geminal silanols, siloxanes, and silanes in most instances. However, it has not been able to distinguish hydrogen-bonded vicinal silanols as a distinct subset of the single silanol category. The requirement of having  $^{29}\text{Si}$  atoms in proximity to protons for NMR detection also provides a degree of surface specificity.

A reactive subset of surface hydroxyls on silica was first proposed by Snyder to be vicinal silanols that contained acidic protons by virtue of hydrogen bonding by an adjacent reactive silanol to the oxygen of the acidic silanol<sup>5</sup>. The acidic properties of silica also have been exploited to determine its surface area via titration with sodium hydroxide. Only a fraction of the silanols are neutralized in going from pH 4 to 9, thus suggesting that the acidic silanols neutralized in this range have some relationship to the postulated subset of reactive silanols.

Underivatized and reversed-phase chromatographic silicas also may possess ion-exchange characteristics<sup>6-8</sup>. Ion-exchange activity can have undesirable effects, for example excessive tailing and low efficiencies during the reversed-phase separation of organic amines<sup>9</sup>. The cation-exchange behavior of silanols in a system will depend primarily on the  $\text{p}K_{\text{a}}$  of the silanols, the solution pH, ionic strength, and composition. The  $\text{p}K_{\text{a}}$  of silanols has been reported to be 9.5 (ref. 10),  $7.1 \pm 0.5$  (ref. 11), and in a range as low as 5-7 (ref. 12). Such a broad range of  $\text{p}K_{\text{a}}$  values reported in the literature for silanols might represent the variability in hydroxyl acidity with structural environment, *i.e.* a median  $\text{p}K_{\text{a}}$  value exists with a significant concentration of more or less acidic silanols.

Previous investigators have shown hydrogen-bonding strength is directly correlated with the acidity of silanols<sup>11</sup> and this is believed to be related to the enhancement of the atomic dipole on the hydrogen-bonded oxygen. Concomitantly, hydrogen bonding enhances the nucleophilicity of the proton donor silanol oxygen atom and this could account for the increased reactivity of some silanols. The strength of a hydrogen bond will depend on the distance between oxygens and on the orientation of the hydrogen to the electron lone-pair orbitals on the hydrogen-bonded oxygen. On a complicated, amorphous surface such as silica, it is easy to envision a range of orientations and distances between hydrogen-bonded hydroxyls and thus a wide range of acidities and reactivities for vicinal silanols.

There is much controversy in the literature about what type of silanol is most reactive<sup>13</sup>. Many investigators claim free or lone hydroxyls are most reactive<sup>14</sup>. Others claim vicinal hydroxyls are most reactive<sup>5,15</sup>, or at least comprise the main adsorption sites<sup>16</sup>. The apparent hydroxyl reactivity will vary with the reagent, but

some of the above-mentioned reports directly contradict each other for the same reagent.

Various experimental techniques have been used to support the above findings, including both chemical and physical methods<sup>13</sup>. However, most of the techniques provide only an estimated mean surface region hydroxyl group concentration. Chemical methods are based upon selective reaction of surface hydroxyl groups to form covalently bound surface species. The idea that surface hydroxyl groups exist mainly as pairs (*e.g.* hydrogen-bonded geminal or vicinal groups) is generally supported by chemical reactions of silica with reagents such as  $\text{AlCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{BCl}_3$ , and  $\text{SiCl}_4$ . However, no clear distinction usually can be made between geminal *vs.* vicinal or lone silanol reactivity. Of the physical characterization methods, infrared (IR) spectroscopy and isotope exchange using deuterated or tritiated water are most common<sup>13</sup>. The fundamental IR region ( $4000\text{--}700\text{ cm}^{-1}$ ) has received the most attention because of strong bands for surface functionalities including lone silanols, hydrogen-bound silanols and deuterated silanols. However, most of these experiments utilize silica plates or pressed pellets with concomitant complications resulting from the physical alteration of particle surfaces and adsorbed water. The overlap of hydrogen-bonded silanol stretching vibrations with those of physically adsorbed water is a particular problem<sup>17</sup>.

The recent application of near-IR techniques involving refractive index matching<sup>17</sup> have advanced the utility of IR for studying surface silanols, water adsorption, and surface reactions including covalent derivatization or isotope exchange. However, no clear distinctions can be made between the relative reactivities of different types of hydrogen-bonded silanol groups<sup>7,17</sup>. This also was the case in a recent  $^{13}\text{C}$  and  $^{29}\text{Si}$  solid-state NMR study of chemically modified silicas<sup>18</sup>. Only single hydroxyl site and siloxane silicons were detected in the  $^{29}\text{Si}$  spectra. The geminal group contribution was not observed, in contrast to prior NMR studies of silica by Maciel and Sindorf<sup>1,3,4</sup>. To investigate these points further,  $^{29}\text{Si}$  solid-state NMR and potentiometric titration are used in this study of the relationship of reactive and acidic hydroxyls on octadecyldimethylsilyl (ODS) reversed-phase silica. Results will be compared with surface chemical and chromatographic data from a previous study on the same silica<sup>7</sup>, in order better to correlate the surface properties with chromatographic behavior.

## EXPERIMENTAL

### *Materials*

ODS reversed-phase substrates were prepared in this laboratory using Whatman Partisil 10 as the starting material. Details about the silica substrate, preparation and characterization of the bonded phases can be found elsewhere<sup>7</sup>.

### *NMR instrumentation*

The solid-state  $^{29}\text{Si}$  CP/MAS NMR spectra were obtained at 39.75 MHz on a modified Nicolet NT-200 spectrometer. Magic-angle sample spinning was maintained at 3.5–4.0 kHz using Delrin rotors of the bullet design. Spectra were the result of coadding between 10,000 and 40,000 acquisitions using a contact time of 2 msec and a pulse repetition rate of 1.0 sec. All chemical shifts were referenced to the silicon

resonance in solid tetra(trimethylsilyl)methane. Spectral bands (geminal and single silanol, and siloxane) were analyzed by the Nicolet curve-fitting program NTC-CAP using a Gaussian peak-shape function<sup>3</sup>.

#### *NMR quantitative procedure*

The surface ODS concentration ( $S$ ) was calculated according to the following equation and is given in units of ODS/nm<sup>2</sup>.

$$S = [1000(\%C)/(77 - (\%C))] \times (N_A \cdot 10^{-21})/[(EMW) (SA)] \quad (1)$$

The %C (combustion analysis) was corrected by subtracting the %C for the blank from each sample. SA is the surface area (BET, nitrogen) of the silica in m<sup>2</sup>/g,  $N_A$  is Avogadro's number, and EMW is the effective molecular weight of the attached ODS which is the weight gain (g/mole) of bound ODS. The 77 factor is due to the fact that 77% of the weight of bound ODS is carbon.

The initial hydroxyl concentration on the blank silica,  $[\text{OH}]^i$ , in -OH/nm<sup>2</sup> was determined using  $S$  and  $f$  parameters.

$$[\text{OH}]^i = (S/f) (1 + f + f_g^r) \quad (2)$$

All  $f$  parameters in this and other equations are obtained from integrated spectral intensities as described elsewhere<sup>3</sup>. The  $f$  term is the ratio of bound ODS silicon atoms to residual silanol silicon atoms and  $f_g^r$  is the ratio of geminal silanol sites to residual silanol sites after the silylation reaction. The  $f_g^r$  value corrects for the presence of two hydroxyl groups per unreacted geminal site.

The initial geminal site concentration ( $G^i$ , geminal site/nm<sup>2</sup>) is calculated by two additional steps. First, the percentage of geminal hydroxyls on the initial silica is calculated using the initial  $f_g$  parameter ( $f_g^i$ ) derived from integrated NMR spectral intensities:

$$\text{fraction of geminal hydroxyls} = [2(f_g^i)]/[2(f_g^i) + (100 - f_g^i)] \quad (3)$$

In the second step,  $G^i$  is determined by multiplying  $[\text{OH}]^i$  by the initial fraction of geminal hydroxyls (eqn. 2 times eqn. 3) and dividing by 2.

The initial single hydroxyl site concentration ( $L^i$ , single OH/nm<sup>2</sup>) is the difference between the total initial hydroxyls and initial geminal hydroxyls.

$$L^i = [\text{OH}]^i - 2G^i \quad (4)$$

The geminal site concentration with an ODS group attached ( $G^r$ ) is the product of  $G^i$  and a second factor.

$$G^r = \theta_g G^i \quad (5)$$

$\theta_g$  is the ratio of reacted geminal sites to initial geminal sites on the surface which is calculated from experimental  $f$  values. Eqn. 5 and all of the other NMR equations assume that only one of the hydroxyls per geminal site can react because of steric reasons.

The residual geminal hydroxyl site concentration after reaction ( $G^u$ ), the concentration of initial single sites reacted with ODS ( $L^r$ ), and the residual single hydroxyl site concentration after reaction ( $L^u$ ) are calculated as follows using previously obtained values for  $G^i$ ,  $G^r$ ,  $S$ ,  $L^i$ .

$$G^u = G^i - G^r \quad (6)$$

$$L^r = S - G^r \quad (7)$$

$$L^u = L^i - L^r \quad (8)$$

The  $\theta$  value is the ratio of reacted geminal and single sites to initial geminal and single hydroxyl sites.

$$\theta = f_g^i \theta_g + (1 - f_g^i) \theta_1 \quad (9)$$

$\theta_1$  is the ratio of reacted single sites to initial single sites and is determined from  $f$  values<sup>3</sup>. The percentage of geminal, single or total hydroxyl sites reacted is simply the corresponding value,  $\theta_g$ ,  $\theta_1$  or  $\theta$  respectively, times 100%.

#### *Surface titrations*

Surface titration of silica was performed using the Sears method<sup>6</sup>, with slight modifications. Instead of an aqueous solution, a methanol-distilled-deionized water (65:35) solution was utilized in order to slurry the reversed-phase silica and duplicate the mobile phase environment used for chromatographic studies. Because the titrations were performed in partially aqueous systems, a correction was applied to the pH reading, [pH(R)], according to the following equation:

$$\text{pH}^* = \text{pH(R)} - \delta \quad (10)$$

The  $\text{pH}^*$  is the corrected reading and the correction  $\delta = 0.15$  (ref. 19). The  $\delta$  value is obtained by comparing the pH meter readings of a standard aqueous buffer and an appropriate partially aqueous buffer. Titration volumes for use in silanol acidity studies were determined from  $\text{pH}^*$  4 to 9.25 in order to maintain a correspondence with titration volumes needed, from pH 4 to 9, of underivatized silica in aqueous solutions. Dissolution of modified silica is negligible at the upper  $\text{pH}^*$  limit. Titrant was added in aliquots of *ca.* 0.1 ml and the solutions were allowed to equilibrate a few minutes after each addition, before pH values were measured.

Acidic surface proton concentration was calculated by dividing the moles of sodium hydroxide at the designated endpoint by the surface area of the silica titrated. This number was then converted to  $\text{H}^+/\text{nm}^2$ . Silica  $\text{p}K_a$  values were estimated by using the  $K_a$  expression and data obtained at the endpoints.

$$K_a = [\text{H}^+][\text{SiO}^-]/[\text{SiOH}] \quad (11)$$

The acidic proton concentration in Table I was used as the surface concentration of  $\text{SiO}^-$ ; the surface hydroxyl concentration was estimated by subtracting the acidic

TABLE I

SURFACE TITRATION AND SURFACE COVERAGE DATA OF WHATMAN PARTISIL 10 DERIVATIZED WITH OCTADECYLDIMETHYLSILANE

<i>Parameter measured</i>	<i>Sample</i>			
	<i>Blank</i>	<i>C<sub>18-I</sub></i>	<i>C<sub>18-II</sub></i>	<i>C<sub>18-III</sub></i>
Protons titrated* (H <sup>+</sup> /nm <sup>2</sup> )	1.69	1.34	1.04	0.78
pK <sub>a</sub> of silanols	9.0	9.2	9.3	9.4
ODS and Na <sup>+</sup> conc. (ODS + Na <sup>+</sup> /nm <sup>2</sup> )	1.69	1.52	1.45	1.60
Percentage surface coverage of Na <sup>+</sup> (Na <sup>+</sup> Å <sup>2</sup> /nm <sup>2</sup> )	40	32	25	19
Percentage surface coverage of ODS (ODS Å <sup>2</sup> /nm <sup>2</sup> )	—	8	19	38
Percentage surface coverage of ODS + Na <sup>+</sup> (ODS + Na <sup>+</sup> Å <sup>2</sup> /nm <sup>2</sup> )	40	40	44	57

\* Reproducibility of the method is 2% relative S.D.<sup>o</sup>.

TABLE II

<sup>29</sup>Si SOLID-STATE NMR DATA ON WHATMAN PARTISIL 10, DERIVATIZED WITH OCTADECYLDIMETHYLSILANE

See Experimental section for details of calculations.

<i>Parameter measured</i>	<i>Sample</i>			
	<i>Blank</i>	<i>C<sub>18-I</sub></i>	<i>C<sub>18-II</sub></i>	<i>C<sub>18-III</sub></i>
<i>Geminal site data</i>				
Geminal site concn. [≡Si(OH) <sub>2</sub> /nm <sup>2</sup> ] = <i>G<sup>u</sup></i>	0.28	0.24	0.15	0.10
ODS on geminal sites (ODS/nm <sup>2</sup> ) = <i>G<sup>r</sup></i>	—	0.045	0.13	0.18
Percentage geminal sites reacted = $\theta_g \times 100\%$	0	16	45	64
<i>Single site data</i>				
Single site concn. (≡SiOH/nm <sup>2</sup> ) = <i>L<sup>u</sup></i>	2.9	2.8	2.6	2.3
ODS on single sites (ODS/nm <sup>2</sup> ) = <i>L<sup>r</sup></i>	—	0.13	0.29	0.64
Percentage single sites reacted = $\theta_1 \times 100\%$	0	4.1	10	25
<i>θ data</i>				
Fraction of -OH sites reacted	—	0.063	0.13	0.29

proton concentration from the residual surface hydroxyl concentration in Table II, and the pH value was used for the  $H^+$  concentration.

## RESULTS AND DISCUSSION

### *Solid-state NMR*

Shown in Fig. 1 are the  $^{29}Si$  NMR spectra for the four silica samples containing

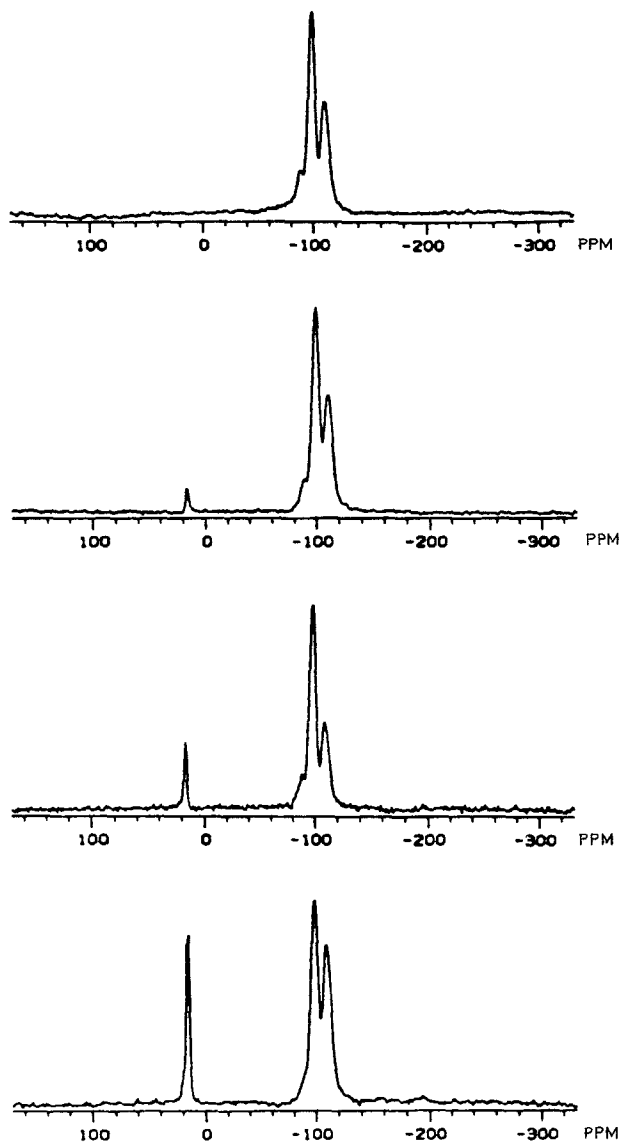


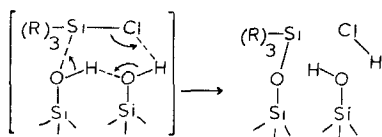
Fig. 1.  $^{29}Si$  solid-state NMR spectra of ODS derivatized silicas (Whatman Partisil 10). From top to bottom the samples are: blank,  $C_{18}$ -I,  $C_{18}$ -II, and  $C_{18}$ -III. The ordinate axis is set to full scale for the largest peak ( $-100$  ppm).

various ODS coverages. The  $^{29}\text{Si}$  resonance at 16 ppm due to silicon atoms present in ODS groups attached to the surface is seen to increase in intensity with ODS coverage as expected. Concurrently, the  $^{29}\text{Si}$  resonance at  $-91$  ppm due to geminal hydroxyl site silicons is seen to decrease relative to the resonance at  $-100$  ppm from single hydroxyl site silicons. The peak at  $-109$  ppm is from siloxane silicons which are near to hydroxyl groups. Siloxanes are difficult to quantify because of their long  $^{29}\text{Si}$ - $^1\text{H}$  cross-polarization relaxation times relative to the silanols. The quantitative  $^{29}\text{Si}$  solid-state NMR data are summarized in Table II. A detailed summary of how these values were calculated is given in the Experimental section.

Examination of Table II and Fig. 2 suggests that as the total surface ODS concentration increases, the total hydroxyl concentration decreases. These concentrations are inversely related in a linear fashion, as expected, with a correlation of  $-0.999$ . However, the number of either geminal or single hydroxyl sites reacted does not increase as linearly with the total ODS content (Fig. 2). The fraction of geminal sites reacted also is much larger than the single sites throughout the range of ODS coverages, suggesting that the available geminal sites react preferentially. Examination of Fig. 2 reveals that the  $\text{C}_{18}$ -III silica appears to approach a limiting ODS-reacted geminal concentration with increasing total ODS content. The ratio of % reacted geminal sites to % reacted single sites has decreased substantially in  $\text{C}_{18}$ -III relative to the lower ODS coverages (Table II, Fig. 2). The fraction of total geminal sites reacted for sample  $\text{C}_{18}$ -III (64%) is close to a maximum value of 65% reported for silica derivatized with trimethylsilyl groups using hexamethyldisilazane<sup>3</sup>. This limit might be due to some steric or geometrical considerations, as suggested in ref. 3, if the surface is composed of sections of 100  $\beta$ -cristobalite with only geminal hydroxyls and 111  $\beta$ -cristobalite with only single hydroxyl sites. The limit of silane concentration could represent a maximum for the 100 face surface composed of only geminal hydroxyls on this particular silica.

If hydrogen-bonding enhances reactivity for vicinal silanols as suggested by Snyder<sup>5</sup>, it is likely that the reactive subset of silanols also includes hydrogen-bonded geminal hydroxyl sites. By using reasonable choices of bond angles and distances it can be shown that the hydroxyls on a geminal silanol are capable of hydrogen bonding to each other. Using a Si-O covalent bond distance of 1.83 Å and a tetrahedral arrangement of 109.5° for the Si-O-Si angle, then the distance between oxygens is 2.99 Å. The critical distance for hydrogen-bonding is 3.1 Å or less, which allows for up to an Si-O-Si angle of 116°.

Snyder proposed that vicinal silanols were more reactive than isolated single silanols with chlorosilanes due to a concerted reaction mechanism involving the reacting hydroxyl as the entering group and a second hydroxyl group to stabilize the leaving chloride group as shown below<sup>20</sup>.





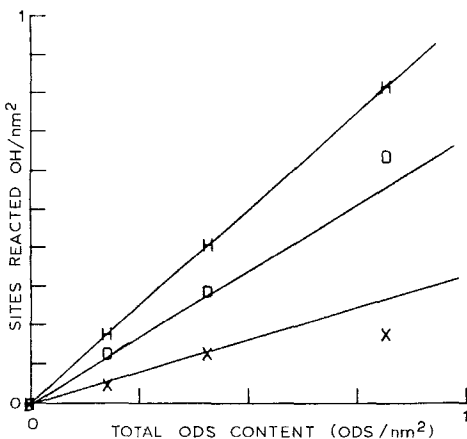


Fig. 2. Types of hydroxyl site reacted ( $-\text{OH}/\text{nm}^2$ ) versus total ODS concentration. Symbols:  $\square$  = single hydroxyl sites;  $\times$  = geminal hydroxyl sites; H = total hydroxyl sites.

Therefore, hydrogen-bonded silanols, in both Snyder's study and the current study of ODS reactions, may have enhanced reactivity with chlorosilanes for three reasons: (1) the second hydroxyl group helps to stabilize the leaving group, (2) hydrogen bonding enhances the nucleophilicity of the reacting hydroxyl, as pointed out above, and (3) the presence of more than one hydroxyl in that region enhances the adsorptive properties.

In summary, the reactive fraction of surface silanols includes a large percentage of the geminal sites (probably up to the limits of reactivity imposed by steric considerations) and a subset of the single sites; probably including various hydrogen-bonded species such as the vicinal silanols. Internal hydrogen bonding between two hydroxyls of a geminal site may contribute to the high reactivity of geminal sites with ODS. However, the explicit fractions of single or geminal sites that are hydrogen bonded can not be calculated directly from NMR data.

#### Comparison of NMR to other techniques

In a previous publication the percentage of total silanols reacted was determined for these ODS samples using transmission near-infrared (NIR) spectroscopy<sup>7</sup>. Shown in Fig. 3 is the percent surface silanols reacted, determined by NMR and transmission NIR, versus ODS coverage. The linear correlations in the plot are 0.999 and 0.993, as determined by NMR and NIR, respectively. The NIR values for the percentage of hydroxyls reacted, however, are systematically higher by 4–5%. Possible reasons for the discrepancy include the following. First, in the transmission NIR procedure the silica must be dried at 150°C to exclude interference from water in the determination. At 150°C a small number of adjacent silanols will start to condense with the simultaneous formation of siloxanes and water. This will result in values of percent hydroxyl reacted that are too high. Secondly, unlike the NIR, the NMR determination does not correct for internal silanols that are inaccessible to the ODS reagent. Thus, the NMR-based percent reacted value may be low. However, it is not expected that the internal silanols will contribute more than a few percent to the <sup>29</sup>Si

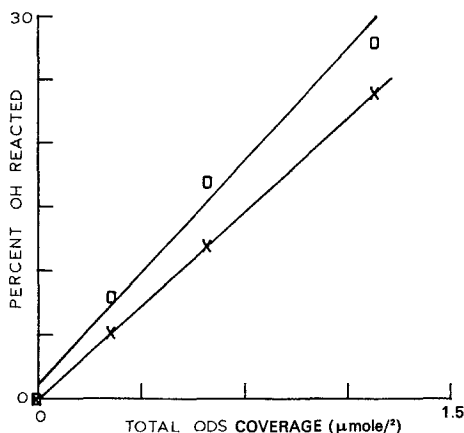


Fig. 3. Percent hydroxyls reacted *versus* ODS coverage. Hydroxyls reacted determined by transmission NIR (□) and solid-state NMR (×). The ODS coverage was determined by percent carbon combustion analysis<sup>7</sup>. The percent hydroxyls from NMR data were computed by dividing the total ODS concentration by the initial hydroxyl concentration to be consistent with the previous method used for NIR quantitation<sup>7</sup>.

signal because previous studies indicate that internal silanol concentrations are low<sup>3,7</sup>.

The initial concentration of surface region hydroxyls on the silica substrate is estimated to be  $5.8 \mu\text{moles}/\text{m}^2$ , as calculated from NMR data using eqn. 2. From extrapolation of the NIR data it was estimated<sup>7</sup> that the initial surface hydroxyl concentration is  $4.9 \mu\text{moles}/\text{m}^2$ . These values agree within 20% and it is expected that the actual value will lie between these numbers owing to the reasons cited above.

The  $\theta$  values listed in Table II represent the ratio of reacted silanol sites to initial silanol sites on the silica surface as determined exclusively from NMR data. Each geminal site counts as only one available hydroxyl site for ODS reaction; thus  $\theta$  is a measure of the surface silane coverage<sup>3</sup>. The  $\theta$  values have a linear correlation *versus* ODS surface coverage, determined from percent carbon combustion data, of 0.998. In a previous publication it was determined that the ODS surface coverage was linearly correlated with quantitation from Fourier Transform IR photoacoustic spectroscopy and X-ray photoelectron spectroscopy<sup>7</sup>. Therefore,  $\theta$  values derived from NMR will also be linearly correlated with quantitation from those spectroscopic techniques over the range of ODS coverages examined.

#### *Surface titration of ODS silica*

To examine the relationship of acidic to ODS-reactive surface silanols, a series of sodium hydroxide titrations of the ODS-reacted silicas were performed. Table I contains the results of the sodium hydroxide surface titration of silanols and corresponding surface coverage data. Fig. 4 shows the acidic proton concentration, determined between  $\text{pH}^* 4$  and 9.25, *versus* the hydroxyl content and total ODS coverage for the four silicas. A lower limit of 4 for  $\text{pH}^*$  was chosen because most of the silanols should be in the protonated form at this value.

The acidic proton content diminishes with decreasing hydroxyl content (in-

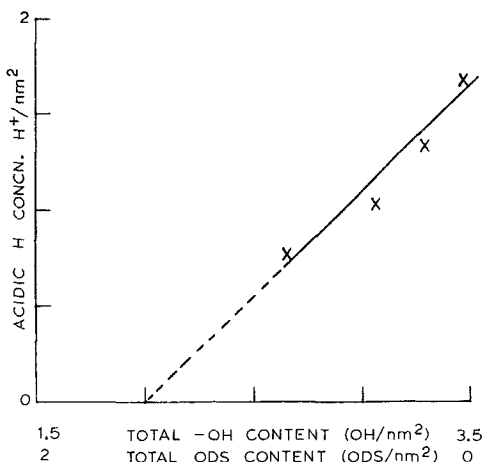


Fig. 4. Acidic surface protons determined by titration *versus* surface silanol concentration determined by solid-state NMR and total ODS coverage determined by percent carbon combustion analysis. Dotted line shows extrapolation to zero acidic  $H^+$  concentration.

creasing ODS content) and this suggests that more acidic protons are lost on silanization of the surface (Table I, Fig. 4). Extrapolation to zero acidic  $H^+$  concentration/nm<sup>2</sup> (Fig. 4) yields a value of 2.0 OH/nm<sup>2</sup> for the “untitratable” hydroxyl content. This value closely agrees with the 1.8 OH/nm<sup>2</sup> value from the difference between the initial hydroxyl concentration derived from NMR data (3.46 OH/nm<sup>2</sup>) and the acidic proton concentration on the untreated silica (1.69  $H^+$ /nm<sup>2</sup>). However, not all of the acidic protons are expected to be ODS-reactable because of steric reasons and the inaccessibility of some silanols which are covered by ODS groups.

It is interesting to note that the sum of titratable (acidic) and silane-reacted (reactive) silanols remains roughly constant as a function of ODS coverage, as shown in Table I. The sum of ODS and  $Na^+$  contents per square nanometre varies over a small range of *ca.* 15%, and this seems to indicate that the ODS-reactive silanols are among the population of acidic silanols on the native silica. If the cross-sectional area of an ODS group is taken as 46 Å<sup>2</sup> (ref. 21) and if a radius of 2.76 Å is used for  $Na^+(aq)$ <sup>22</sup> to estimate a circular cross-section of 24 Å<sup>2</sup>, then a surface coverage of ODS and  $Na^+(aq)$  can be calculated. The total surface coverage of ODS and  $Na^+(aq)$ , from Table I, is approximately the same for the blank, C<sub>18</sub>-I, and C<sub>18</sub>-II at 40% coverage. However, the coverage for C<sub>18</sub>-III is somewhat higher (57%) and thus indicates that the surface accessibility is probably not the only barrier to silanol reactivity at lower ODS coverages. Several factors probably contribute to the overall limits in the coverage of ODS +  $Na^+(aq)$ . The first possibility is simply a decrease in the residual silanol acidity or reactivity, which is consistent with the apparent rise calculated for the  $pK_a$  value of the silanol as a function of ODS coverage (Table I). Secondly, if the surface distribution of hydroxyl groups is inhomogeneous, so that they tend to occur in clusters, then many of the silanols may be inaccessible due to masking by previously bound surface ODS and  $Na^+$  species. This second point will be addressed later in the discussion.

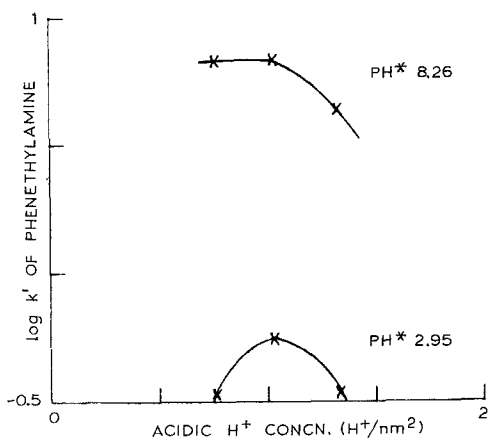


Fig. 5. Log  $k'$  of phenethylamine *versus* acidic surface proton content determined by titration of samples C<sub>18</sub>-I, C<sub>18</sub>-II and C<sub>18</sub>-III.

#### *Comparison with chromatographic behavior*

In a previous publication it was stated that these ODS silicas exhibited ion-exchange behavior in chromatographing a basic solute, phenethylamine<sup>7</sup>. Fig. 5 shows a plot of log capacity factor ( $k'$ ) of phenethylamine *versus* acidic proton concentration for the three ODS silicas. A chromatographic mobile phase of methanol-water (65:35) with phosphate buffers at pH\* 8.26 or 2.95 was employed. For the pH\* 8.26 experiment, the log  $k'$  appears to increase slightly and then level off as the acidic proton concentration decreases. It is expected that the log  $k'$  would decrease with a drop in acidic proton concentration if retention was limited by the number of hydroxyl groups that participate in ion exchange. The observed increase in log  $k'$  with the accompanying drop in plate number<sup>7</sup>, suggests that the change in retention with ODS coverage is due more to the inaccessibility of silanols<sup>9</sup>. This is further substantiated by the slower reaction of sodium hydroxide with the highest coverage of ODS-reacted silica. It required over 5 h to reach the endpoint in the titration of C<sub>18</sub>-III, the silica with the highest ODS coverage and the lowest efficiency for phenethylamine, while other silica samples were titrated to the endpoint in *ca.* 2 h, even though more titrant was required to reach the designated endpoints.

Also shown in Fig. 5 is the retention behavior of phenethylamine, with a mobile phase pH\* of 2.95, *versus* acidic proton concentration. The retention in this case suggests a bimodal mechanism. At pH\* 2.95, silanols will have limited ion-exchange capabilities owing to their tendency to remain in the protonated form. However, amines can still have silanophilic interactions such as hydrogen bonding, as well as hydrophobic interactions in this environment. Therefore, it is postulated that under these conditions the behavior of phenethylamine is dependent on a dual retention mechanism involving silanophilic and hydrophobic interactions. Apparently, the contribution of each mechanism varies with the ODS coverage.

It may seem surprising that phenethylamine has trouble penetrating the ODS overlayer to access silanols, when a maximum of only 38% of the surface area is covered by ODS groups. In a previous publication<sup>7</sup> it was postulated that ODS groups predominantly occur as clusters or aggregates on the silica surface which

resulted in a partition-like behavior for some liquid chromatographic separations. It appears that silanols may also occur as clusters instead of being homogeneously distributed on the surface. This would help explain the formation of ODS groups into aggregates, which would tend to mask the residual silanols of the cluster and limit phenethylamine's accessibility to some silanols. It was observed previously that the retention of some non-polar and polar solutes was pH dependent, which was apparently due to restructuring of the alkyl chains<sup>7</sup>. If some of the residual silanols are underneath the ODS aggregates, then this view would also account for the importance of residual silanol ionization in determining the orientation of overlying alkyl chains to allow for solvation of the surface charge.

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#### REFERENCES

- 1 G. E. Maciel and D. W. Sindorf, *J. Amer. Chem. Soc.*, 102 (1980) 7606-7607.
- 2 D. W. Sindorf, *Ph.D. Dissertation*, Colorado State University, Fort Collins, CO, June, 1982.
- 3 D. W. Sindorf and G. E. Maciel, *J. Phys. Chem.*, 86 (1982) 5208-5219.
- 4 D. W. Sindorf and G. E. Maciel, *J. Amer. Chem. Soc.*, 105 (1983) 1487-1493.
- 5 L. R. Snyder, *Separ. Sci.*, 1 (1966) 191-218.
- 6 G. W. Sears, *Anal. Chem.*, 28 (1956) 1981-1983.
- 7 M. L. Miller, R. W. Linton, S. G. Bush and J. W. Jorgenson, *Anal. Chem.*, 56 (1984) 2204-2210.
- 8 G. W. Weber and W. G. Tramposch, *Anal. Chem.*, 55 (1983) 1771-1775.
- 9 B. A. Bidlingmeyer, J. K. Del Rios and J. Korpl, *Anal. Chem.*, 54 (1982) 442-447.
- 10 R. E. Majors, in Cs. Horváth (Editor), *High-Performance Liquid Chromatography —Advances and Perspectives*, Vol. 1, Academic Press, New York, 1980, p. 78.
- 11 M. L. Hair and W. J. Hertl, *J. Phys. Chem.*, 74 (1970) 91-94.
- 12 B. L. Karger, J. N. LePage and N. Tanaka, in Cs. Horváth (Editor), *High-Performance Liquid Chromatography —Advances and Perspectives*, Vol. 2, Academic Press, New York, 1980, p. 133.
- 13 K. K. Unger, *Porous Silica —Its Properties and Use as Support in Column Liquid Chromatography*, Elsevier, Amsterdam, New York, 1979.
- 14 D. J. C. Yates, G. W. Dembinski, W. R. Kroll and J. J. Elliott, *J. Phys. Chem.*, 73 (1969) 911-921.
- 15 J. Kunawicz, P. Jones and J. A. Hockey, *Trans. Faraday Soc.*, 67 (1971) 848-853.
- 16 J. J. Fripiat and J. Uytterhoeven, *J. Phys. Chem.*, 66 (1962) 800-805.
- 17 S. G. Bush, J. W. Jorgenson, M. L. Miller and R. W. Linton, *J. Chromatogr.*, 260 (1983) 1-12.
- 18 E. Bayer, K. Albert, J. Reiners, M. Nieder and D. Müller, *J. Chromatogr.*, 264 (1983) 197-213.
- 19 D. D. Perrin and B. Dempsey, *Buffers For pH and Metal Ion Control*, Chapman and Hall, London, 1974, pp. 79-80.
- 20 L. R. Snyder and J. W. Ward, *J. Phys. Chem.*, 70 (1966) 3941-3952.
- 21 P. Larsen and O. Schou, *Chromatographia*, 16 (1982) 204-206.
- 22 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 4th ed., 1980, p. 255.