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Nuclear Magnetic Resonance Measurements of Line Width, Chemical Shift, and Intensity for Molecules Adsorbed on Silica*

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Summary

High-resolution NMR spectra were taken of molecules adsorbed on silica to determine the effects of specific surface interactions on line widths, chemical shifts, equilibria, and freezing points. Line widths were measured for cyclohexane, benzene, acetone, and methanol adsorbed at monolayer coverage. Hydrogen bonding to the surface was evident for the latter two compounds from the decrease in line width when the silica was silanized. In addition, the hydroxyl hydrogen of methanol was found to undergo exchange with the surface. After silanization, chemical-shift changes were noted for cyclohexane, *p*-xylene, mesitylene, acetone, and methyl acetate. Attempts were made to explain the magnitude of the changes by comparison with data from infrared spectroscopy and gas–solid chromatography. Chemical shifts of mixtures of adsorbates were studied to gain additional information on relative adsorption strengths. The tautomeric equilibrium of adsorbed acetylacetone was measured from the relative integrated intensities of the keto and enol resonances. The enol form was favored more on silanized silica than on hydrated silica. Relative intensities were also used to study the freezing of adsorbates.

High-resolution NMR has been used to study the adsorption of molecules at low surface coverages on wide-pore silicas with the aim of investigating specific interactions that are commonly encountered in

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adsorption chromatography. Cyclohexane, benzene, acetone, and methanol were chosen as representative adsorbates, because the strength of interaction of these compounds with a hydroxylated silica surface is known to vary from weak to strong, as has been shown by measurements of heats of adsorption (*1*), surface hydroxyl stretching frequency shifts (*1*), and gas-chromatographic retention volumes (*2*). Cyclohexane is adsorbed only by nonspecific dispersion forces, whereas benzene forms weak hydrogen bonds with surface silanols via its π-electrons, and the other compounds form strong hydrogen bonds. It was anticipated that these differences in adsorption strength might be reflected in the adsorbate line widths and chemical shifts. For example, Geschke (*3*) found upfield chemical shifts, relative to the pure liquids, for cyclohexane and water adsorbed on a porous silica gel. The shift for water was greater than that for cyclohexane, and it was suggested that these shifts were proportional to the relative adsorption strengths.

In the present study, pyrogenic silica (Cab-O-Sil) was used for most of the experiments for reasons outlined previously (*4*). Effects of specific interactions were studied by varying the surface hydroxyl concentration. After preliminary NMR data showed that adsorbate line widths were insensitive to the drying temperature (from 25–400°C) of Cab-O-Sil, it was decided to look at effects of larger changes in the hydroxyl content of the surface. Two possibilities were available. One was drastic dehydroxylation of the surface at 1000°C. However, this was undesirable because sintering increases agglomerate size, with a consequent increase in inhomogeneous broadening and a probably decrease in pore size. The alternative was silanization of the surface, a technique commonly used in gas chromatography to deactivate silanol sites. This reaction has been studied by Babkin et al., who measured isotherms for several compounds adsorbed on Aerosil and found that silanization considerably reduced the adsorption capacity (*5, 6*). Silanization was chosen for the present experiments because it did not change the bulk properties of the surface area of Cab-O-Sil, because it changed the character of the surface from hydrophilic to hydrophobic, and because there is current interest in the properties of similar surface-modified silicas (*7, 8*).

One of the advantages of narrow-line adsorption spectra, as opposed to relaxation times, is that mixtures of adsorbates having different chemical shifts can be studied. In the present work, mixtures of cyclohexane, acetone, and methanol were used to investigate competition between adsorbates for surface sites. In another part of this study, monolayers of solutes were added to solid supports that had been coated with high-molecular-weight partitioning liquids of the type used in gas–liquid chromatography (GLC). Although supports (such as diatomaceous earth) commonly used for GLC are not suitable for such an NMR study because they have intolerably high levels of paramagnetic impurities and such small surface areas that detection of a monolayer of adsorbate would be impossible, Cab-O-Sil or Syloid 72 can be used. Those adsorbents, when coated with a stationary liquid phase, constitute typical lightly-loaded supports. Support surface effects on solute retention behavior have been reported for similar supports having ten or fewer layers of stationary phase (*9*), and it was anticipated that changes in the concentration of stationary phase would be reflected in the solute spectra.

In addition to line widths and chemical shifts, integrated intensities have also been found useful for studying adsorbate properties such as equilibria and freezing points. Karagounis and Gutbrod (*10*) were the first to report the use of intensities for measuring equilibria in their study of the monomer–trimer equilibrium of paraformaldehyde adsorbed on silica. In the present study, which had been completed before the work of Karagounis and Gutbrod had come to our attention, the tautomeric equilibrium of acetylacetone has been measured on hydrated and on silanized Cab-O-Sil.

Acetylacetone (2,4-pentanedione) was chosen on the basis of the following known facts from its solution behavior (*11, 12*). The methyl resonances of the keto and enol forms have a chemical shift difference of ca. 0.16 ppm, represent six equivalent protons, and are not significantly exchange-broadened. The equilibrium position is known to change dramatically with solvent character because the keto form is polar and is capable of forming intermolecular hydrogen bonds with proton donors, whereas the enol form, which is known to possess a strong intramolecular hydrogen bond, is relatively nonpolar (*13*).

A brief IR study by Yoshino (*14*) had indicated that the enol percentage, when adsorbed on silica, was smaller than that of the pure liquid. Unfortunately, absolute enol contents could not be determined by IR measurement because the relative absorptivites of the enol and keto carbonyl vibrations were not known. In contrast, absolute numbers should be attainable by NMR, along with information on the variation of the equilibrium with temperature.

Integrated intensities can also be used to study freezing-point depression upon adsorption, which has been observed over the years by several workers using a variety of experimental techniques (e.g., Refs. *15,16*). The freezing behavior of substances adsorbed on heterogeneous surfaces has been characterized by (a) larger depressions in narrow pores than in wide pores, (b) larger depressions at low surface coverages than at high coverages, and (c) gradual freezing over a range of temperatures. Berezin (*17*) recently employed a thermodynamic approach to calculate the fraction of adsorbate remaining unfrozen at a given temperature, coverage from known values of the slope of the isotherm at that temperature, and the isosteric heat of adsorption at that coverage.

Freezing points of adsorbed molecules are easy to follow by high-resolution NMR because, when a compound freezes, its resonance line becomes too broad to detect. In an application of Berezin's approach (*17*), it was that that freezing points in the adsorbed state for a series of compounds showing different degrees of specific interaction with silica could be compared in a study similar to that of Karagounis (*18*), who found an increase in freezing-point depression with the number of π-electrons in a series of aromatic compounds adsorbed on tin.

The present study also included some IR and gas–solid chromatographic (GSC) measurements in order to try to establish relations among the data obtained from NMR, IR, and GSC. IR spectroscopy was used to measure the magnitude of the frequency shift of isolated surface silanols upon adsorption of molecules having different electronic structures. Other workers have made similar studies and have attempted to correlate the shifts with the degree of specific interaction. [See the reviews of Little (*19*) and Hair (*20*).] Recently, Hertl and Hair found that the correlations could be improved by dividing adsorbates into three classes: saturated and aromatic hydrocarbons, compounds having lone-pair electrons in *p*-orbitals, and compounds having lone pairs in hybrid orbitals (*21*). Changes in the intensity and frequency of bands due to the adsorbates themselves have also been studied for a few molecules, such as benzene (*22*), and were used in the present work to investigate adsorbed acetone and acetonitrile.

Kiselev et al. (*2*) have done gas chromatography with hydrated and dehydrated wide-pore silica and have attempted to correlate retention volumes with IR silanol frequency shifts ($\Delta\nu_{OH}$) and differential heats of adsorption (ΔH). Relatively little GSC work has been done with pyrogenic silicas although their nonporous surface and high purity should be attractive features. A major drawback has been the inconvenience of working with extremely fine particles that create an excessive pressure drop across a packed column. Halasz and Gerlach (*23*) overcame this problem by making packed capillaries. In the present study, an alternative approach has been used so as to prevent subjecting the silica to high temperatures before use.

EXPERIMENTAL

Apparatus

The NMR system and method of sample preparation have been described previously (*4*). A Varian C-1024 time-averaging computer was used for ensemble averaging. IR spectra were taken on a Perkin-Elmer 421 spectrometer. Gas-chromatographic measurements were made with the apparatus described by Oberholtzer and Rogers (*24*).

Reagents

The silicas used were Cab-O-Sil MS-7 (Cabot Corp., Boston, Mass.) and Syloids 72 and 65 (Davison Chemical Co., Baltimore, Md.). The surface of Cab-O-Sil is reported to be only about 50% hydroxylated (*25*), whereas the Syloids were nearly fully hydroxylated. Syloid 72 was a wide-pore gel having a surface area of 370 m^2/g (*26*). Both Syloids had 4-μ diameter particles and were treated with hydrochloric acid to reduce the level of iron impurity. The properties of Cab-O-Sil have been described previously (*4*).

The adsorbates used were reagent grade, when available, and contained no impurities detectable by NMR. Hexamethyldisilazane (HMDS) was obtained from Applied Science Laboratories, State College, Pa. Partitioning liquids used were Carbowax 20M (Analabs, Inc., Hamden, Conn.) and squalane (Distillation Products Industries, Rochester, N.Y.).

Procedures

Silicas were silanized by evacuation for 2 hr at 400°C followed by reaction with HMDS vapor at 400°C for 4 hr in a closed vessel. The HMDS reacted with surface hydroxyls to form trimethylsilyl ethers on the surface with elimination of water (*7*).

Solids and partitioning liquids were adsorbed by dissolving a known amount in an appropriate solvent, adding a known weight of silica, mixing, and allowing the solvent to evaporate slowly.

All NMR data were taken at 40°C unless otherwise specified.

For the relative line-width experiment, two sample tubes of adsorbent were prepared for each adsorbate. After evacuating the silica in the tubes at room temperature, adsorbates were added and spectra were taken. The silica was then dried in the tubes at the next higher temperature, adsorbates were added again, etc. The silica was also silanized in the sample tubes.

For chemical-shift measurements, external referencing was used in order not to contaminate the samples. The external reference liquids were kept in separate precision-ground thin-wall tubes, and their spectra were recorded immediately after the sample spectra. The tubes were of such quality that cyclohexane in five different tubes had the same chemical shift within 0.5 Hz. When relative shifts of several adsorbates were compared, each compound was run on two tubes of hydrated Cab-O-Sil and two tubes of silanized Cab-O-Sil. The same tubes of packed adsorbent were used for all the compounds to eliminate any differences in chemical shift due to variations in packing density. Adsorbate shifts were corrected for diamagnetic susceptibility using the method described previously (*4*).

Samples of acetylacetone on Cab-O-Sil were equilibrated at the experimental temperature in a constant temperature water bath for 6 hr prior to each set of measurements. Successive scans of a sample were accumulated on the time-averaging computer to increase the signal-to-noise ratio. The analog output of the computer was recorded on chart paper. Also, the individual channel contents were digitized with a system consisting of a Hewlett-Packard 3460A digital voltmeter and Tally 1588/420 paper tape punch. The digital data were processed on a Hewlett-Packard 2116A computer. Enol percentages were calculated from the relative integrated intensities of the keto and enol resonances. Unfortunately, the resonance lines overlapped in several cases, so that deconvolution was necessary in order to calculate an accurate area ratio.

Two approaches to deconvolution were used. In one, a DuPont 310 Curve Resolver was employed to deconvolute the analog data, using Lorentzian curve shapes. The relative areas were precise to ±5% except in cases where the relative heights were greater than 4:1 or the peak separation was as small as the full width at half-maximum height. In the second approach, digital data were processed by subtractive deconvolution, using the fourth-derivative program of Morrey (*27*) to locate the two peak centers. In the subtractive method, it was assumed that the overlap of the two resonances was such that the area under the outer half of a given resonance line contained no contribution from the other line. Therefore, when the outer half of a given line was pivoted about the peak center and subtracted from the total area, the remaining area was that due to the second peak. This method was evaluated using synthetically generated Lorentzian curves having approximately the same relative areas and degrees of overlap as the experimentally obtained spectra. When the correct peak centers were used, the relative areas were accurate to ±2%. However, the fourth-derivative method had difficulty (as did the Curve Resolver) locating the exact center of the smaller peak in situations where the ratio of heights was large and/or the peaks were fused. In those cases, the over-all accuracy of the relative areas was reduced to ±12%.

Samples for IR spectroscopy were prepared by pressing silica powder into transparent pellets (ca. 15 mg/cm^2), drying the pellets at any temperature up to 400°C in a vacuum cell similar to that of Angell and Schaffer (*28*), and adding the desired pressure of adsorbate vapor. The mean position of the adsorption band was used when measuring frequencies of adsorbate bands that did not have sharp maxima (e.g., the carbonyl stretching vibration of acetone).

Pelletized Cab-O-Sil for gas chromatography was prepared by soaking Cab-O-Sil in carbon tetrachloride, evaporating off the solvent, carefully crushing the resulting cake, and collecting particles in the 30–70 mesh range. These large agglomerates packed easily into a 0.19-cm i.d. × 15-cm glass column and prevented excessive pressure drop across the column. The column was conditioned overnight at 130°C, using helium carrier gas.

Data were digitized and processed as described by Oberholtzer and Rogers (*24*). Retention times were computed from the peak means, not the maxima. Although a sample-size dependence, typical of GSC on heterogeneous adsorbents, was noted for most of the compounds, sample sizes in the range from the minimum detectable up to five times that amount usually had retention times that agreed within 0.2%.

After completing studies on the hydrated surface, the Cab-O-Sil was silanized in the column by successive injections of liquid HMDS at 200°C, and the experiment was repeated. IR spectra of the column contents showed that this method of silanization was just as effective

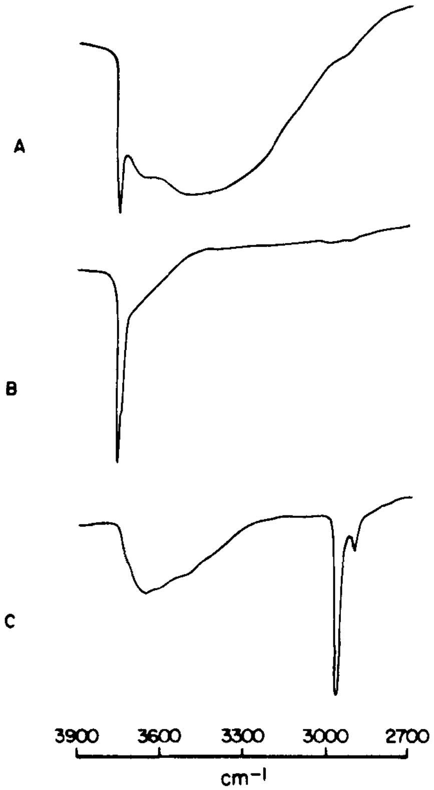

FIG. 1. IR spectra of Cab-O-Sil. (A) After evacuation at 125°C. (B) After evacuation at 400°C. (C) After silanization at 400°C.

as the 400°C vacuum treatment. All peaks were slightly-to-moderately skewed [skew parameter (*29*) of 0.3–1.0] on both the hydrated and silanized surfaces. HETP values ranged from 0.1–0.5 cm.

RESULTS

IR Spectra of Silica Surfaces

IR spectroscopy has provided information about the nature of the hydroxyl groups on silica that will be helpful to know before the NMR data are discussed. The hydroxyl stretching region of the IR spectrum of Cab-O-Sil is shown in Fig. 1. After evacuation for 4 hr at 125°C, a strong sharp band attributed to isolated surface hydroxyls appeared at 3750 cm^{-1}, due to the incomplete hydroxylation and nonporous nature of the Cab-O-Sil surface. [For a discussion of the assignments of frequencies to different types of hydroxyls, see the reviews of Little (*19*) and Hair (*20*).] In addition, broad bands due to hydrogen-bonded hydroxyls occurred at 3650 and ca. 3400 cm^{-1}. There was no detectable amount of molecular water on the surface as judged by the absence of a band at 1630 cm^{-1}, but the remaining surface was clearly heterogeneous.

After evacuation at 400°C, most of the hydrogen-bonded hydroxyls had been removed, leaving only isolated hydroxyls at 3750 cm^{-1} and a few weakly bound hydroxyls at lower frequencies. Treatment of this sample with HMDS yielded the bottom spectrum in which the C—H stretching bands of the chemisorbed trimethylsilyl groups were visible at 2950 cm^{-1}. (These groups were not detectable using the NMR spectrometer.) Also, notice that some bound hydroxyls remained. Apparently they were unreactive toward the silane reagent, perhaps for steric reasons. The fact that silica cannot be completely silanized is now quite well recognized (*7, 30*).

The IR spectrum of Syloid 72 after evacuation at 400°C showed a broad band at 3650 cm^{-1} without resolution of the isolated hydroxyls at 3750 cm^{-1}. Such a spectrum is characteristic of gels having pore diameters in the vicinity of 200 Å (*30*). The number of hydroxyls remaining after silanization appeared larger on Syloid 72 than on Cab-O-Sil. Spectra of Syloid 65 were not taken because that silica could not be pressed into a transparent disk.

NMR Line Widths

Specific Interactions. The purpose of this experiment was to determine if there was a correlation between adsorbate line width and specific interaction strength. Preliminary results with Cab-O-Sil were somewhat disappointing, because cyclohexane, benzene, and acetone all had the same line width (3 Hz), within experimental error. The methyl resonance of methanol was broader (6 Hz), and the hydroxyl resonance was undetectable (as was that of water at monolayer coverage) due to exchange with the surface. Furthermore, none of the line widths changed when the surface was evacuated at 400°C or silanized.

Two possible explanations can be offered for the insensitivity of the line widths to adsorption strength. First, there may have been no differences in the relaxation times, for there is no *a priori* reason why changes in adsorption strength must be reflected in adsorbate mobility.

Second, changes in the transverse relaxation time (T_2) may have occurred, but the corresponding line-width changes may have been small enough to be masked by the inhomogeneous broadening (*4*). If the latter situation were true, then a more hydroxylated surface might permit greater differentiation of the compounds. On this hypothesis, the experiment was repeated with Syloid 72.

The Syloid results are shown in Table 1. For a given surface treatment, the line widths of cyclohexane and benzene were identical, within experimental error, whereas that of acetone was significantly broader and that of methanol was much broader. Therefore line width on this silica increased with the strength of hydrogen bonding.

TABLE 1

Line Widths (Hz)[a] on Syloid 72 at $\theta = 1$

Adsorbate	Surface treatment Evac. (25°C)	Evac. (200°C)	Evac. (400°C)	HMDS (400°C)
Cyclohexane	9.6	9.2	10.5	9.5
Benzene	10.0	10.4	10.8	9.0
Acetone	13.0	13.8	12.8	10.5
Methanol (CH_3)	23	22	18	12.5

[a] Values are averages of measurements on duplicate samples. Individual sample were reproducible to ±1 Hz.

The influence of silanization can be found in the same table. Cyclohexane was unaffected by silanization, as expected, since it cannot form hydrogen bonds. The change, if any, in benzene line width was too small to be detected with certainty. However, acetone showed a reduction in line width on the silanized surface, where the hydrogen bonding capability was reduced, while methanol showed a sensitivity to the drying temperature of the hydrated silica as well as to silanization. Those results can be rationalized on the basis of the findings of Borello et al. (*31*), who proposed that the maximum number of hydrogen bonds that can be formed per methanol molecule changes from three on a fully hydrated surface to two on a sparsely hydrated surface or to one on a methylated surface. In the last case, hydrogen bonding to the surface ether linkage can occur because methanol is a proton donor as well as acceptor. Note that the methyl line width of

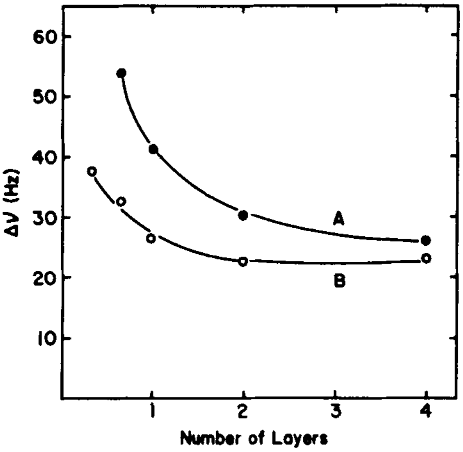

FIG. 2. Effect of silanization on the methyl resonance of methanol adsorbed on Syloid 65. (A) Hydrated surface. (B) Silanized surface.

methanol on the silanized surface was greater than the line widths of the other three adsorbates.

The differences in behavior found on Cab-O-Sil and Syloid lend support to the reactive silanol theory of Snyder (*32*). Since the IR spectra showed that Cab-O-Sil could be silanized more completely than Syloid, one might have expected to see greater line width changes due to silanization on Cab-O-Sil than on Syloid. However, the opposite was true. Snyder and Ward (*30*) found that the concentration of the most reactive sites ("reactive silanols") for specific physical adsorption increased with decreasing pore diameter, being very low on Cab-O-Sil. If this is true, the concentration of "reactive" silanols would be higher on Syloid than on Cab-O-Sil, even though the total number of silanizable hydroxyls was greater on Cab-O-Sil, and hence the greater line-width differentiation with Syloid.

This hypothesis suggested examination of narrower-pore gels having higher concentrations of "reactive" hydroxyls. Figure 2 shows data for methanol on hydrated and on silanized Syloid 65. Note the considerable difference in the methyl line width at monolayer coverage. Note also that the line-width difference diminished with surface coverage, since at higher coverages the over-all effect of the surface was reduced.

Benzene line widths on Syloid 65 were unaffected by silanization. This result is consistent with the pulse-echo data of Michel (*33*), who found that increasing the drying temperature from 100 to 400°C did

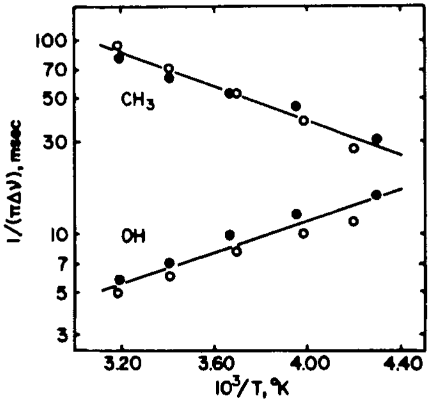

FIG. 3. Methanol adsorbed on Cab-O-Sil, $\theta = 3$. (●) Hydrated surface. (○) Silanized surface.

not affect the relaxation times of adsorbed benzene. Both he and Woessner (*34*) neglected interaction terms with surface hydroxyls in their theoretical treatments of the relaxation of benzene on silica.

Exchange Broadening. As mentioned above, the hydroxyl resonance of methanol was too broad at monolayer coverage to be detected at 40°C. However, at three-layer coverage a broad line appeared whose width could be measured after signal averaging. Upon decreasing the temperature, the hydroxyl line width decreased while the methyl line with increased, as shown in Fig. 3. Similar hydroxyl behavior has been reported for methanol on porous silica (*10*) and for water on Aerosil (*35*) and indicates an exchange process involving the hydroxyl groups.

It was of interest to try to determine what type of exchange process was occurring since, for the methanol–Cab-O-Sil system, several mechanisms could be envisioned. In addition to exchange between bulk methanol molecules having the same chemical shift (the process that causes collapse of spin-spin coupling in the pure liquid), interaction could occur with surface hydroxyl protons, with other surface oxygen atoms, or with a strongly bound layer of methanol molecules having a different chemical shift from the outer layers. If the exchange were with surface hydroxyls, a further complication would arise from the fact that the transverse relaxation time of a proton in a surface hydroxyl group is much shorter than that of a proton in an adsorbed methanol molecule. Therefore, the line broadening could be due to an averaging of relaxation times, as found by Clifford and Lecchini for water on Aerosil (*35*), and be independent of the existence of any chemical-shift difference.

Initially it was thought that the exchange reaction might be eliminated by silanizing the surface. However, this procedure failed to cause any change in the line widths (Fig. 3). That result suggested that either the remaining bound hydroxyls or the ether linkages on the trimethylsilyl groups or on siloxane groups also serve as exchange sites.

Further information was obtained from the temperature behavior of the methyl resonance. In the pure liquid, this resonance was split into a doublet at temperatures below 0°C. When the liquid was made 10^{-4} *M* in hydrochloric acid, the doublet just collapsed at —20°C, due to acid catalysis of the exchange rate. No doublet was observed for adsorbed methanol at that temperature. Although the line for the adsorbed species was too broad to have given good resolution of the doublet if it had been present, the presence of spin-spin coupling should have been detectable as an additional broadening of the observed line. The absence of the doublet agrees with the known surface acidity of silica. For example, Cabot Corporation reports a pH of 3.6–4.2 for a 5% aqueous suspension of Cab-O-Sil (*36*). The apparent short lifetime of a hydroxyl proton on a given methanol molecule at —20°C suggests that the broader hydroxyl lines observed at higher temperatures may have been due to an averaging of T_2 values.

The chemical-shift difference between the methyl and hydroxyl resonances was also measured. This difference was equal to that of the pure liquid at temperatures below 0°C, but was 5–6 Hz less than that of the pure liquid at 40°C. This was true on both the hydrated and silanized surfaces. These results are reasonable if the resonance frequency of the surface site is upfield from the resonance frequency of adsorbed methanol hydroxyls. At low temperatures only the hydroxyl signal from slowly exchanging methanol molecules would be seen, while at higher temperatures (faster exchange rates) the observed shift would be a concentration-weighted average of the shifts for the two or more sites.

In conclusion, it is apparent that the exchange behavior is complex and cannot be elucidated fully without other information. A detailed NMR analysis was prohibited by the poor signal-to-noise ratio of the methanol hydroxyl group and the inability to observe the resonance of the surface group.

Chemical Shifts

Specific Interactions. Chemical shifts of several adsorbates on hydrated and silanized Cab-O-Sil are given in Table 2. Compounds in

TABLE 2

Chemical Shifts (ppm)[a] on Cab-O-Sil at $\theta = 1$

Adsorbate	Silanized	Hydrated	Silanized-hydrated
Cyclohexane	−.09	−.09	.00
Cyclohexene (CH, CH_2)	−.08, −.06	−.15, −.06	.07, .00
Acetone	.00	−.08	.08
Methyl acetate (OCH_3, $COCH_3$)	−.04, .00	−.08, −.06	.04, .06
Methanol (CH_3)	−.05	−.06	.01
Benzene	−.48	−.47	.01
p-Xylene (Ar, CH_3)	−.30, −.32	−.39, −.36	.09, .04
Mesitylene (Ar, CH_3)	−.34, −.31	−.45, −.37	.11, .06
Nitromethane	.02	.02	.00
Acetonitrile	.00	.02	.02

[a] Shifts are relative to the pure liquids, after correction for diamagnetic susceptibility. A negative sign means a downfield shift from the neat liquid. Values are averages of measurements on duplicate samples and were reproducible to ±0.02 ppm. Differences less than 0.03 ppm were considered to be within experimental uncertainty of zero.

addition to those used for the line-width study were chosen to give a broader selection of types of specifically interacting functional groups. Contrary to Geschke's results (*3*), no large upfield shifts were noted. Except for the aromatic compounds, the variation from compound to compound in the magnitude of the corrected shift has no obvious significance. Possible reasons for these small variations might be either adsorbate densities that were different from the liquid values (*37*) or dilution shifts.

The data of most significance are the differences in chemical shift on the two surfaces, because these differences should be indicative of hydrogen bonding of adsorbates to surface hydroxyls. For cyclohexane, the chemical shifts were the same on hydrated and silanized Cab-O-Sil. This result was expected because the adsorption on each surface should have been only of the nonspecific type. For cyclohexane, the alkene hydrogens were shifted 0.07 ppm downfield on the hydrated surface relative to the silanized surface. This indicates a deshielding of those hydrogens due to π-electron interaction with surface hydroxyls. Since no change was observed for the aliphatic hydrogens, the change on the hydrated surface can safely be attributed to an electronic interaction rather than to different adsorbate densities on the two surfaces. Similar downfield shifts on the hydrated surface were observed for acetone and methyl acetate, both of which form hydrogen bonds with surface silanols through the carbonyl group.

The lack of a change for methanol was consistent with the finding that its hydroxyl hydrogen underwent exchange on both surfaces. Therefore, the electronic environment of the methyl group was probably similar in each situation.

The aromatic compounds showed large downfield shifts, previously reported by Geschke (*3*), which can be attributed to a dilution effect since similar behavior has been observed in dilute solution. These shifts are reported to be a consequence of the aromatic ring current with maximum deshielding being realized at infinite dilution (*38*). Hence, benzene adsorbed at monolayer coverage would appear to be in a very dilute state. Note that although there was no difference in the benzene chemical shift on the two surfaces, there were differences for the methyl-substituted benzenes. The fact that the difference increased with the number of methyl groups suggests that the strength of the hydrogen bond to the surface may have increased.

Contrary to expectation, no differences in chemical shift on the two surfaces were observed for acetonitrile or nitromethane. These compounds have also been shown to hydrogen bond to silica (see later discussion), so an explanation for the lack of chemical shift change was needed. For this reason, solvent shifts were measured.

Solute chemical shifts vs internal tetramethylsilane (TMS) were measured at 5 and 1% concentrations in carbon tetrachloride (dielectric constant, $\epsilon = 2.2$), methanol ($\epsilon = 33.6$), nitromethane ($\epsilon = 35.0$), and dimethylsulfoxide ($\epsilon = 46$). These concentration levels bracketed the concentrations of the adsorbed molecules at monolayer coverage. In all cases, the chemical shifts were the same at the two concentrations.

The solvent shifts of the following molecules are in good agreement with the adsorbate shifts in Table 2. Cyclohexane had the same shift in carbon tetrachloride and in methanol. The alkane hydrogens of cyclohexane were insensitive to solvent polarity, whereas the chemical shift for the alkene hydrogens in the polar solvents was 0.03–0.07 ppm downfield from the carbon tetrachloride value. The chemical shifts of acetone and methyl acetate in methanol were 0.08 and 0.05 ppm downfield from those in carbon tetrachloride, but the shifts in nitromethane and dimethylsulfoxide were the same as in carbon tetrachloride. Apparently the acetone and methyl acetate shifts were more sensitive to hydrogen bonding than to changes in the dielectric constant of the solvent.

The solvent shifts of the other compounds did not parallel the adsorbate shifts. For benzene, the shifts relative to the pure liquid were further downfield (0.20 ppm) in the polar solvents than in carbon tetrachloride (0.12 ppm), but still far less than the reported infinite dilution shift (0.70 ppm) in carbon tetrachloride (*39*) or the shift in the adsorbed state (0.47 ppm). Either the monolayer of benzene was effectively more dilute than a 1% solution or the anisotropy in the adsorbed phase (*34*) caused a change in the shielding constant. Mesitylene behaved similarly. The chemical shifts of acetonitrile and nitromethane were also sensitive to solvent polarity, being 0.07 and 0.10 ppm downfield from the carbon tetrachloride values in methanol and dimethylsulfoxide solvents, respectively. Therefore, it was surprising that no differences were observed on hydrated and silanized Cab-O-Sil, unless the two surfaces were of similar polarity and the chemical shifts were insensitive to changes in hydrogen bonding.

Mixtures of Adsorbates. Chemical shifts of a monolayer of acetone in the presence of cyclohexane or methanol are shown in Table 3. The 0.08 ppm difference in chemical shift on hydrated vs silanized Cab-O-Sil was not destroyed by one or ten layers of added cyclohexane, but it was destroyed by one layer of methanol. These data suggest that cyclohexane did not compete with acetone for surface sites, but methanol did compete successfully for surface sites and made the silanized surface appear to acetone like a hydrated surface. Qualitatively, the line widths also supported that conclusion. For a 1:1 cyclohexane:acetone mixture on hydrated Cab-O-Sil, the cyclohexane line width was only half that of acetone, whereas for a 1:1 methanol:acetone mixture, the line widths were practically equal.

TABLE 3

Chemical Shifts (ppm) of Acetone[a] Adsorbed on Cab-O-Sil in the Presence of Other Adsorbates

Surface	Acetone ($\theta = 1$)	Acetone:cyclohexane 1:1	Acetone:cyclohexane 1:10	Acetone:methanol 1:1	Acetone:methanol 1:10
Silanized	0	0	+0.07	−0.10	−0.10
Hydrated	−0.08	−0.10	−0.07	−0.10	−0.10

[a] Corrected for the diamagnetic susceptibility of the system.

Spectra were also taken of monolayer amounts of cyclohexane or methanol added to Syloid 72 having 20% w/w coatings of squalane or Carbowax 20 M. The Carbowax resonance was too broad to be detected at 40°C. The resonance lines of squalane were detected, but they did not interfere with those of cyclohexane or methanol. Measurements on these samples showed that the solute line widths were far more sensitive to the amount of physically adsorbed water on the silica surface than to the presence of the high-molecular-weight coating. Later studies in which the coated supports were dried first at 125°C failed to show any meaningful differences in solute line width on the coated support relative to the bare support. Apparently the surface effect on solute line width dominated any effect due to the two or three layers of stationary phase. Use of larger amounts of stationary phase was avoided to prevent operating in regions of high-coverage broadening. Therefore it was not feasible to attempt additional studies aimed at isolating contributions from gas–liquid partitioning and gas–solid adsorption.

Integrated Intensities

Equilibria. Values for the percentage of enol tautomer of acetylacetone adsorbed on Cab-O-Sil between 25 and 80°C are shown in Fig. 4. Although there is scatter in the data, general trends are detect-

TABLE 4

Percent Enol at 45°C and Thermodynamic Data Obtained by NMR

System	Percent enol[a]	$-\Delta H$ (kcal/mole)[b]	$-\Delta S^c$ (e.u.)
Hydrated Cab-O-Sil, $\theta = 2$	70.6	3.3 ± 4%	8.6 ± 0.8
$\theta = 1$	69.4	3.2 ± 7%	8.4 ± 1.5
Silanized Cab-O-Sil, $\theta = 2$	76.0	1.2 ± 28%	1.5 ± 2.0
$\theta = 1$	82.2	1.6 ± 23%	2.0 ± 2.0
Pure liquid	73.2	2.7 ± 5%	6.5 ± 0.8
1% solution in water[d]	12.3	2.3 ± 46%	11.1 ± 6.7
1% solution in dioxane[d]	76.7	4.5 ± 7%	11.8 ± 2.0

[a] Uncertainty estimated to be ±3 percent enol in all cases.

[b] Uncertainty is relative standard deviation of least-squares line.

[c] Uncertain is range of values, based on uncertainty in ΔH values.

[d] From reference *(12)*.

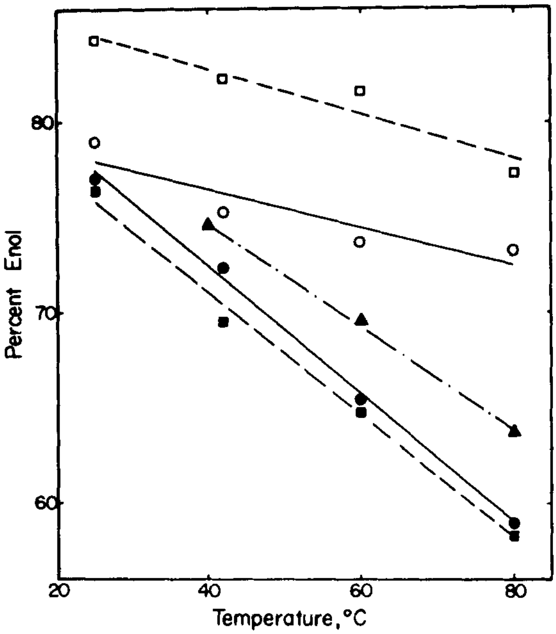

FIG. 4. Acetylacetone adsorbed on Cab-O-Sil. Each point is the average of results obtained by both analog and digital deconvolution methods on each of two duplicate samples. Filled symbols: Hydrated surface. Open symbols: Silanized surface. Circles and solid lines: $\theta = 2$. Squares and dashed lines: $\theta = 1$. Triangles: Neat acetylacetone.

able. First, the enol content was higher on the silanized surface than on the hydrated surface. Second, there was a surface-coverage dependence on the silanized surface but not (within experimental error) on the hydrated surface. Third, the change of equilibrium with temperature was in the normal direction, the enol percentage being larger at lower temperatures (*12*).

Table 4 shows values of the percent enol at 45°C for the diketone in the adsorbed state and in solution. Although the changes in percent enol with coverage and surface type were quite small, they appear to be significant and can be explained with reference to the solution values. For example, on the silanized surface, which contains hydrocarbon groups, the percent enol was higher than that of the pure liquid and quite similar to that in the nonpolar solvent dioxane ($\epsilon = 2.2$). Furthermore, the percent enol was higher at monolayer coverage than at two-layer coverage. On the hydrated surface, which contains silanol groups, the percent enol was smaller than that in the pure liquid and in the direction of (though not close to) the value in water ($\epsilon = 80.4$). These data suggest that the equilibrium might be governed by the relative polarities of the surfaces. Alternatively, the greater abundance of the keto form on the hydrated surface may be due to a favorable hydrogen-bonding interaction which cannot take place on the silanized surface. A decision between these two hypotheses cannot be made without other data.

Enthalpies of tautomerization, which were obtained from the slopes of plots ln (enol/keto) vs $1/T$ are also shown in Table 4. The heat of tautomerization found for the pure liquid was identical to the value found by Reeves (*40*). The enthalpies and entropies on the hydrated surface were slightly larger than the liquid values, and those on the silanized surface were significantly smaller (i.e., less negative). Hence, the conversion of keto to enol was apparently less favorable on the silanized surface. Since the mechanism for conversion involves protonation of a keto oxygen followed by loss of an alpha hydrogen to yield an ion which electronically rearranges to the enol (*41*), the low entropy on the silanized silica could reflect the paucity of proton acceptor sites (e.g., lone-pair electrons).

As a check on the results obtained by NMR spectroscopy, an attempt was made to determine relative changes in the acetylacetone equilibrium by IR measurements. This was possible because the carbonyl stretching frequencies of the keto and enol tautomers were sufficiently different (1720 and 1630 cm^{-1}, respectively) to permit measurement of the ratio of absorbances. Only relative changes in equilibrium could be measured because it was not possible to obtain the separate absorptivities of the keto and enol absorption bands.

As seen in Table 5, the trend of the IR data was the same as that found by NMR; namely, the percent enol was higher on the silanized surface than on the hydrated surface. The small differences between the two sets of values can be attributed to unequal absorptivities and/or to the fact that the temperature of the sample in the IR measurements was not known and may have been higher than 45°C, due to heating by the undispersed IR beam. In addition, the sample dried at 400°C (leaving only isolated surface hydroxyls) gave the same result as that dried at 125°C, indicating that the degree of surface hydroxylation had much less effect on the equilibrium than the presence of the trimethylsilyl groups. The enol percentages on the hydrated silica were considerably higher than those inferred from Yoshino's data (*14*).

TABLE 5

Percent Enol and Frequency Shifts Obtained by IR

Cab-O-Sil surface	Drying temp. (°C)	Silica ν_{OH} (cm^{-1})		Percent enol	
		Before adsorption	After adsorption	IR ($\theta = 3/4$)	NMR ($\theta = 1$)
		3750			
Hydrated	125	3675	3400	62	69
Hydrated	400	3750	3400	62	—
Silanized	125	3675	3420	77	82

Although the frequencies of the carbonyl bands in the adsorbed keto and enol forms were the same, within experimental error, as for the liquid values, the frequency shifts of the surface hydroxyl stretching vibrations indicated a hydrogen-bonding interaction with the adsorbed diketone. Even the relatively unreactive hydroxyls on the silanized surface were shifted to about the same frequency (3400 cm^{-1}), as shown in Table 5. The magnitude of these shifts is similar to that found by Hertl and Hair (*21*) for adsorbed acetone. (See later discussion.)

It was hoped that NMR could also be used to study hindered rotation of adsorbed molecules just as Kiselev et al. (*42*) had used IR to study the rotamer equilibrium of 1,2-dichloroethane on Aerosil. As in exchange experiments, the separate resonances from a pair of rotamers should collapse when the rate of interconversion is close to the difference in their chemical shifts. In the case of 1,2-dichloroethane, the interconversion rate was too rapid to permit observation of the separate resonances at easily attained temperatures. However, compounds having coalescence temperatures above room temperature, such as *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and *N*,*N*-dimethylnitrosoamine, looked more promising. Nevertheless, at monolayer coverage on hydrated Cab-O-Sil, no changes in coalescence temperature were observed. Either adsorption did not alter the energy barriers for interconversion or the changes of coalescence temperature were too small to be detected.

Freezing Points. For adsorbed monolayers of several compounds at temperatures above their normal freezing points, comparison of adsorbate signal areas with the areas of solutions of equivalent concentration showed that all of the adsorbed material was detected. That is, there was no evidence that a portion of adsorbate was adsorbed too strongly to give a detectable signal.

However, as temperatures were lowered below the normal freezing points, a gradual loss of integrated intensity occurred, as shown in Table 6 for benzene (mp 5.5°C) adsorbed on Cab-O-Sil. The freezing-point depression was greatest at $\theta = 1$ and decreased with coverage. Nevertheless, the freezing point of adsorbed benzene at $\theta = 30$ was still lower than that of pure benzene. Derouane (*43*) has suggested that only the volume in micropores should freeze below the normal value. According to his interpretation, Cab-O-Sil would necessarily have a micropore volume that was not yet filled at $\theta = 30$.

TABLE 6

Freezing Behavior of Benzene Adsorbed on Cab-O-Sil

	Percentage of unfrozen liquid[a]			
Temp. (°C)	$\theta = 1$	$\theta = 3$	$\theta = 15$	$\theta = 30$
6	100	100	100	100
−3	100	100	100	100
−9	100	100	30	5
−18	95	90	15	0
−36	65	27	8	0

[a] Based on relative integrated intensities.

An attempt was made to measure freezing-point ranges for a series of compounds with the hope of relating the freezing-point depressions to heats of adsorption. However, a suitable series of compounds having similar melting points (preferably in the range 50–100°C), uncoupled resonance lines, and a large number of equivalent protons could not be found. As shown in Table 6, the freezing point of benzene adsorbed at low coverage was too low to be measured. So was that of *t*-butanol (normal mp 25.5°C). Also, the resonance line of water at monolayer coverage was too broad to detect with a high-resolution instrument. For those reasons, higher-melting compounds which are normally solids at room temperature were examined. This worked well for hexamethylbenzene (normal mp 160°, depression 90°) and cyclododecane (normal mp 61–63°, depression 50°). However, suitable polar analogs were not readily available. Neither were the heats of adsorption of the compounds.

Other Studies of Adsorbates

Gas–Solid Chromatography was performed in order to gain a better understanding of the nature of the hydrated and silanized surfaces and to try to explain some of the chemical shifts reported in Table 2. Kiselev and coworkers measured ratios of retention volumes on hydroxylated and dehydroxylated wide-pore silica for a series of compounds and found that the ratios were roughly proportional to the hydrogen bonding contributions to the heats of adsorption (*2*). In the present study it was of interest to determine if silanization had the same effect as Kiselev's thermal dehydration (1000°C).

The compounds used are arranged in Table 7 in the order of elution

TABLE 7

Data from GSC and IRS

Compound	bp (°C)	k_h/k_s[a] (126°C)	$-\Delta H_h$[b] (kcal/mole)	$-\Delta H_s$[b] (kcal/mole)	$\Delta\nu_{OH}$[c] (cm^{-1})
Cyclohexane	81.4	1.75[d]	8.2 ± 10%	8.7 ± 0.1%	45[e]
Cyclohexene	83	3.12	10.9 ± 10%	8.5 ± 0.1%	220[f]
Benzene	80.1	5.15	12.1 ± 14%	7.9 ± 2.4%	126[g]
Nitromethane	101	8.40	14.0 ± 14%	10.8 ± 0.8%	160[g]
Methanol	64.6	3.4[h,i]	—	—	—
Acetonitrile	82	10.9	13.1 ± 4%	12.3 ± 6%	300[g]
p-Xylene	138.3	9.12	—	—	154[g]
Mesitylene	—	—	—	—	172[g]
Methyl acetate	57.1	39.0[h]	15.0 ± 6%	13.7 ± 7%	270[f]
Acetone	56.5	41.4[h]	16.4 ± 7%	13.8 ± 6%	345[e]

[a] Quotient of GSC capacity ratios on hydrated (k_h) and silanized (k_s) surfaces.

[b] Heats of adsorption on hydrated (ΔH_h) and silanized (ΔH_s) surfaces. Uncertainty is relative standard deviation of least-squares line.

[c] IR shift of surface silanol frequency.

[d] Nonunity ratio indicates greater nonspecific interaction energy on hydrated surface. See reference (*6*).

[e] From reference (*21*). Duplicated in the present study.

[f] This study.

[g] From reference (*1*). Duplicated in the present study.

[h] Retention time was measured with a stopwatch.

[i] Peaks were badly tailed on both surfaces.

from the column of hydrated Cab-O-Sil. Examination of the data shows that the elution order was no simple function of boiling point. This was expected because all of the compounds, except cyclohexane, adsorb specifically on surface silanols. On the silanized column, the elution order followed the boiling points, except for acetonitrile, methyl acetate, acetone, and methanol, which were retained about 30% too long. The extra retention of those four compounds, which can form strong hydrogen bonds with surface silanols, indicates that a small number of specific adsorption sites remained. Neverthless, the quotients of capacity ratios, k_h/k_s, on the two surfaces emphasize the drastic reduction in retention of polar compounds that resulted from silanization. The relative values of the quotients are basically in agreement with Kiselev's results (*2*).

Heats of adsorption determined from GSC data are also shown in Table 7. On the hydrated surface, the enthalpies increased on going down the series of compounds and, except for nitromethane, are in fair agreement with those reported by Galkin et al. (*1*). On the silanized surface, the enthalpies were generally smaller (the same, within experimental error, for cyclohexane) than on the hydrated surface, but still increased upon going down the series. On the contrary, Davydov et al. had found that the enthalpies for hexane, benzene, acetonitrile, nitromethane, and acetone on dehydroxylated silica were all in the range 8.5–9.9 kcal/mole (*44*). Therefore, the present heats of adsorption indicate that compounds with strong hydrogen-bonding capability interacted with residual hydroxyls on the silanized surface, a conclusion reached earlier by examination of the elution order.

Infrared Spectroscopy. Values of the silanol frequency shift ($\Delta\nu_{OH}$) for several compounds adsorbed on Cab-O-Sil (or its equivalent, Aerosil) are also shown in Table 7. Generally the shifts were larger for compounds that formed strong hydrogen bonds with the surface than for compounds that showed only weak specific interactions. Within the series of substituted aromatics, good correlations of $\Delta\nu_{OH}$ with ionization potential have been reported (*22, 45*). The differences in chemical shift (hydrated vs silanized Cab-O-Sil) for those same compounds increased in the same order as the $\Delta\nu_{OH}$ values. Similarly the $\Delta\nu_{OH}$, chemical shift change, and quotient of capacity ratios were all larger for acetone than for methyl acetate. Certain discrepancies exist, however. If one uses the quotients of capacity ratios as measures of specific adsorption strength, the $\Delta\nu_{OH}$ value for cyclohexane was larger than that predicted from the $\Delta\nu_{OH}$ values for the aromatic compounds, and the value for acetonitrile was too large relative to the values for nitromethane and acetone.

Shifts of IR bands associated with an adsorbate itself were also measured. For acetone, the carbonyl frequency was 1705 cm^{-1} on the hydrated silica and 1716 cm^{-1} on the silanized silica, precise to ±2 cm^{-1}. Those frequencies were lower than the liquid value (1738 cm^{-1}), as noted by others (*46*). The important fact is that the frequency was lower on the hydrated surface than on the silanized one. This result is consistent with the chemical-shift data and indicates a greater withdrawal of electron density from the C=O bond on the hydrated surface (due to hydrogen bonding) than on the silanized surface.

IR studies of other adsorbates were not as successful. The C≡N band of acetonitrile showed no significant frequency shift upon adsorption, a result in agreement with the data of Geodakyan et al. (*47*) and consistent with the chemical-shift data. However, it was inconsistent with chromatographic and IR $\Delta\nu_{OH}$ data. Geodakyan et al. (*47*) proposed that acetonitrile did hydrogen bond with the surface and that the lack of change in the nitrile frequency was due to the noncharacteristic nature of the vibration. Cyclohexene could not be studied because the intensity of the double-bond stretching mode was too weak. For nitromethane, the N—O bands were intense, but no significant changes in frequency were noted upon adsorption.

DISCUSSION

Activity of Surface Sites

Data obtained in the present study, as well as that already in the literature, leave some confusion about the activity of the residual hydroxyls on silanized silica. The capacity ratios, chemical shifts, and line widths suggest that the silanized surface was much less active than the hydrated surface. However, the elution order on the silanized GSC column, the heats of adsorption obtained by GSC, the large IR $\Delta\nu_{OH}$ caused by acetylacetone on silanized Cab-O-Sil, and the exchange processes occurring with adsorbed methanol all indicate a significant residual population of hydroxyls that were capable of reacting with adsorbates. However, the two sets of observations are not as contradictory as they appear if one considers the relative adsorption strengths of different types of hydroxyl sites and also the kinetics of adsorption. Snyder and Ward (*30*) found that reactive and isolated hydroxyls were silanized rapidly, but that there was a slow reaction with the remaining hydroxyls after the fast reaction had been completed. In addition, exchange of deuterium oxide was reported to be rapid at room temperature with free hydroxyls and slower with bound hydroxyls (*48*). Recent IR studies showed that water could absorb on both free and bound hydroxyls (*49*), but that adsorption took place preferentially on the free hydroxyls (*50*). Babkin and Kiselev (*6*) assumed that methanol and water could hydrogen-bond to residual hydroxyls in order to explain the isotherms and heats of adsorption on silanized Aerosil. It is not unreasonable, then, that adsorption could have occurred on residual hydroxyls on a silanized surface when other more active sites were not available, even though the kinetics of adsorption might have been slower.

Relative Strengths of Specific Interactions

Although some correlations were made among data obtained by NMR, IR, and GSC, exceptions to trends were prevalent. For example, determination of the relative specific interaction strengths of nitromethane and acetonitrile was particularly troublesome. On the other hand, difficulties should be expected because each method measures different molecular properties and types of motion (translational, vibrational, or rotational). Distinctions must be made between measures of kinetic properties (e.g., line widths) and measures of thermodynamic properties (e.g., capacity ratios and heats of adsorption). In addition, some parameters reflect interactions of an entire molecule, whereas others deal only with a particular functional group. most of these considerations have been presented earlier. They will now be used to rationalize some of the observed discrepancies.

When comparing data on specfic surface interactions obtained by different methods, one of the problems is finding a suitable reference property. Heat of adsorption would seem to be a logical choice although there is disagreement between Galkin et al. (*1*) and Hertl and Hair (*21*) about the magnitude of the contribution from specific interactions. The relative capacity ratios will be used in the following discussion because they paralleled heats of adsorption more closely than did other data.

The decreases in NMR line width upon silanization indicated the following order of specific interaction strengths; methanol > acetone > benzene = cyclohexane = 0. This order parallels the heats of adsorption, although the latter indicate a weak specific interaction for benzene. However, caution must be exercised when interpreting the line widths of alcohols and other exchangeable species. For example, the observation that the hydroxyl line width of methanol was much greater than the methyl line width at 40°C does not necessarily support the hypothesis of Geschke and Pfeifer (*51*) that the hydroxyl group is adsorbed closer to the surface than the methyl group. By extrapolation of the data in Figure 3, the line widths would be equal at about —55°C.

Chemical-shift differences on hydrated and silanized Cab-O-Sil showed the following trend: mesitylene > acetone = cyclohexene > methyl acetate > benzene = nitromethane = acetonitrile = 0. In several respects, this sequence disagrees with the GSC sequence: acetone > methyl acetate > acetonitrile > nitromethane > benzene > cyclohexene. The near equivalence of the chemical-shift differences for mesitylene, acetone, and cyclohexene can be rationalized by noting that the hydrogen atoms are closer to the interacting π-system in mesitylene and cyclohexene than they are in acetone, so a proximity effect may be operating. From the GSC data, one would predict smaller differences for benzene, nitromethane, and acetonitrile than for acetone, but some change would still be expected in view of the large shift for cyclohexane. A possible explanation for these results is that the chemical shifts for benzene, nitromethane, and acetonitrile were influenced by changes in the dielectric constant of the surrounding medium but not by hydrogen bonding, whereas the chemical shift of acetone was strongly influenced by hydrogen bonding but not appreciably by polarity changes. The solvent shifts support that hypothesis. The hydrogen-bonding donor capacities of hydrated and silanized Cab-O-Sil were very different, but the polarities were not markedly different, according to the acetylacetone data. If the hypothesis is correct, the chemical shifts for cyclohexane and mesitylene must have been strongly influenced by hydrogen bonding.

Relative magnitudes of $\Delta\nu_{OH}$ values from the IR experiment suggested the following sequence of specific interaction strengths: acetone > acetonitrile > methyl acetate > cyclohexane > nitromethane > benzene. However, considering the results of Hertl and Hair (*21*) and the fact that the lone pair of electrons on the nitrogen atom in acetonitrile is in a hybrid orbital (*52*) rather than a *p*-orbital, the heat of adsorption of that compound should be lower than the $\Delta\nu_{OH}$ value suggests. When that correction is made, the IR data are in agreement with the GSC data, except for the relative adsorption strengths of cyclohexane and benzene.

From the above discussion it is apparent that comparison of NMR line-width and chemical-shift changes is not a reliable method for establishing relative strengths of specific interaction for widely different types of compounds. As with IR frequency shifts for surface silanols, correlations should be limited to homologous series or to closely related compounds. In such cases, chemical-shift measurements at higher field strengths and lower surface coverages might make it possible to observe more subtle interactions.

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