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Effects of Adsorbent Properties on Nuclear Magnetic Resonance Line Widths of Adsorbates*

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Summary

An analytical NMR spectrometer has been used to measure line widths of molecules adsorbed on silica so as to investigate the capabilities and limitations of such measurements. Comparisons of line widths with transverse relaxation times (T_2) for the same samples showed that the observed resonance lines were inhomogeneously broadened. Consequently, line widths are not a reliable way of obtaining T_2 values or activation energies. The porosity of silica appeared to be an important factor governing adsorbate line widths, the narrowest lines being observed with adsorbents having the largest pore diameters. The narrow resonance lines observed for molecules adsorbed at low coverages on pyrogenic silica have been attributed to the nonporous surface, small particle size, and high purity of that adsorbent. Broadening of lines at high surface coverages on pyrogenic silica appeared to be due to slow exchange of molecules between surface and bulk states having different chemical shifts. Potential applications of high-resolution NMR to the study of gas–solid adsorption are outlined.

Continuing interest in silica as a chromatographic adsorbent is apparent from a survey of the recent literature. For example, Kiselev (*1*) has investigated types of surface interactions that occur in gas–solid chromatography and has been especially concerned with the specificity of adsorbate–adsorbent interactions, the effects of surface

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modifications, and the nature of the adsorbed phase. Snyder (*2*) has studied liquid–solid chromatography with the goals of correlating types of surface sites with retention behavior and of understanding how the sites and their relative activities are affected by activation and deactivation of the adsorbent.

One of the numerous methods employed to study adsorbed molecules is nuclear magnetic resonance spectroscopy. Most previous NMR studies have been made by the pulse-echo technique, in which the longitudinal and transverse relaxation times (T_1 and T_2, respectively) of the adsorbates have been measured by application of a series of rf pulses to the sample. From measurements of the relaxation times as a function of temperature, detailed observations of molecular motions, phase changes, exchange processes, and activation energies have been made (*3*, *4*).

To date, the only adsorbates on silica for which detailed relaxation-time measurements have been made are water (*5*, *6*) and benzene (*7–9*). It would be of interest to chromatographers to have NMR data for the adsorption, on a given silica, of several small molecules that exhibit different strengths of specific interaction (e.g., hydrogen bonding) with the adsorbent surface. To the authors' knowledge, no such data are presently available in the literature.

In an earlier communication (*10*) it was reported that analytical high-resolution NMR spectrometers looked promising for studying molecules adsorbed on pyrogenic silica, because the adsorbates had narrow resonance lines. Although a high-resolution spectrometer permits measurement of only one of the two relaxation times that can be determined by the pulse-echo technique, it has the advantage of giving chemical shift information. In addition to measuring relative linewidth and chemical-shift changes upon adsorption, one should also be able to study mixtures of adsorbates and adsorbates having more than one resonance line, as long as the resolution is adequate. Variable temperature studies could be expected to yield information about activation energies and phase changes.

Before embarking upon such studies, it was necessary to investigate two questions that were left unanswered in the previous report (*10*). First, why were the observed line widths strongly dependent on the type of silica used? Since one would like to relate line widths to the relaxation behavior of an adsorbate, it was important to determine whether certain characteristics of the adsorbent (e.g., purity, particle size, pore size) contributed to the observed line width. Second, why

did the resonance lines broaden at high surface coverages (30–50 layers)? This phenomenon also needed further investigation, because it would be desirable to be able to study molecules at high coverages (e.g., coated supports for gas–liquid chromatography) as well as at monolayer coverage.

The present paper is concerned with (a) a careful evaluation of the validity of line-width data, (b) properties of the adsorbent that affect adsorbate line widths, and (c) an alternative explanation for line broadening at high surface coverages. Capabilities of a high-resolution NMR spectrometer for studying adsorbed molecules and limitations on the types of systems that can be studied are also discussed. In the following paper (*11*), NMR measurements are presented for several molecules adsorbed on wide-pore silicas, and the NMR data is correlated with data from infrared and gas–solid chromatographic measurements.

Line widths of samples containing solid particles may contain contributions from other factors in addition to the nuclear relaxation of the adsorbate. The presence of paramagnetic ions in silica can cause an undesirable shortening of T_1 by electron spin–nuclear spin interactions. This effect has been well documented by Michel in pulse-echo studies of water (*6*) and benzene (*7*) on silica and has been avoided to a great extent in the present work by using silicas having a low iron content. Even when that factor has been eliminated, measured line widths may not correspond to transverse relaxation times according to the theoretical relation

$$\Delta\nu = 1/(\pi T_2)$$

Gesche (*12*) has shown that this relation was not obeyed for cyclohexane, benzene, and water adsorbed on a porous silica. He found that the line widths were inhomogeneously broadened relative to the T_2 values, in some cases by as much as a factor of twelve. Inhomogeneous broadening has also been observed in powdered metal samples (*13, 14*).

It was thought that the narrower lines observed with pyrogenic silica relative to precipitated silicas (*10*) might be due primarily to the absence of internal pores in the former adsorbent. However, little attention has been given in previous studies to the effect of adsorbent porosity on the NMR spectra of adsorbed molecules. German workers have noted two-phase relaxation for water on alumina (*15, 16*) and for benzene on porous silica (*8*), and they have suggested that the two phases were liquid in micropore and macropore regions. Clifford and

Lecchini (*17*) found that T_1 and T_2 for fifteen layers of adsorbed water were shorter on a microporous silica gel than on a macroporous gel. However, data from different laboratories for adsorbed benzene are conflicting. For example, Geschke (*12*), Michel (*9*), and Woessner (*7*) reported values of 136, 400, and 5 msec, respectively, for about a monolayer of benzene adsorbed on porous silicas having reportedly similar characteristics. Unfortunately, no one has reported a systematic pulse-echo study of a series of silicas of different porosity using standard conditions of adsorbate, coverage, and pretreatment. In the present study, line widths have been measured for a monolayer of cyclohexane adsorbed on a series of silicas having widely different pore sizes. Cyclohexane was chosen as the adsorbate because it is known to exhibit only nonspecific interactions with silica (*1*) and should be affected less than other adsorbates by variations in the type or concentration of surface hydroxyls.

EXPERIMENTAL

Apparatus

High-resolution NMR spectra were obtained using a Varian A-60 spectrometer equipped with a V-6040 variable temperature controller. Relaxation times were measured at an independent laboratory using a Magnion pulse-echo spectrometer operated at 40 MHz. T_1 values were measured with 180–90° pulse sequences; T_2 values were measured by the Carr-Purcell method.

Reagents

Cyclohexane, benzene, and methanol were spectrophotometric grade. Other adsorbates were reagent grade.

The silica adsorbents were of two types, pyrogenic and precipitated. The pyrogenic silica was Cab-O-Sil MS-7 (Cabot Corp., Boston, Mass.), which consists of chainlike agglomerates of highly pure, nonporous spheres having an average diameter of 12 mμ (*18*).

A high-purity precipitated silica, E-1, was synthesized by slow hydrolysis of ethyl orthosilicate, yielding a narrow-pore gel. Silica F-1 was prepared by rapid gelation of sodium silicate in the presence of 0.15 *M* sodium fluoride, yielding a wide-pore gel (*19*). The dried gel particles were ground gently in an alumina mortar to a size that would pass through a 400-mesh sieve. Nitrogen surface areas and pore vol-

umes of these two gels were measured by a static BET technique at an independent laboratory.

Analyses for iron and aluminum were made using standard spectrophotometric 1,10-phenanthroline (*20*) and 8-quinolinol (*21*) procedures, respectively. The results, along with other physical properties, are summarized in Table 1.

TABLE 1

Properties of Silicas

Silica	Fe content (ppm)	Al content (ppm)	Mean particle diameter (μ)	Packing density (g/cm^3)	Nitrogen surface area (m^2/g)	Pore volume (cm^3/g)	Mean[a] pore diameter (Å)
Cab-O-Sil	3	33	0.012	0.12	200	6.0[b]	1200
F-1	7	25	<37[c]	0.34	235	2.1[d]	220
E-1	2	12	<37[c]	0.77	600	0.66[d]	24

[a] Pore diameter = 4 (pore volume)/(surface area).
[b] Total pore volume, measured by saturation with benzene.
[c] Through 400-mesh sieve.
[d] Nitrogen micropore volume.

In addition, three Davison silica gels (Davison Chemical Co., Baltimore, Md.), grades 58, 81, and 40, were used. Because these had higher iron contents, they were boiled in concentrated hydrochloric acid for several hours to reduce the iron level below 25 ppm. Nitrogen surface areas, measured by the flow technique of Nelsen and Eggertsen (*22*), were 285, 520, and 530 m^2/g, respectively.

Procedures

Samples for NMR spectroscopy were prepared by adding weighed amounts of silica to 5-mm o.d. polished thin-wall sample tubes (Wilmad Glass Co., Buena, N.J.). Normally, centrifugation (3600 rpm) was used to pack the silica to a constant density. With the pyrogenic silica, which had a low bulk density, further packing with a glass rod was desirable in order to increase the amount of sample present in the sensitive area of the spectrometer probe and to prevent shrinkage of adsorbent when large amounts of adsorbate were added. After drying the packed silica for 12 hr at 125°C, liquid adsorbate was added to the side of a tube with a microsyringe and allowed to equilibrate with the adsorbent for 2–3 days. Surface coverages, θ, were cal-

culated from the surface areas and literature values of molecular cross-sectional areas (*23*). The θ values are only estimates, due to uncertainties in cross-sections and lack of isotherms for the particular systems studied.

For samples having line widths greater than 10 Hz, rapid spinning (ca. 10,000 rpm) was necessary in order to get data that were independent of spinning rate. Line widths ($\Delta\nu$) are reported as the full width at half-maximum height. The precision (range) of line-width measurements on a given sample was ± 0.5 Hz or $\pm 10\%$, whichever was larger. Reproducibility of line widths of a given adsorbate at a fixed coverage on different tubes of adsorbent was ± 1 Hz. Precision of relaxation times was $\pm 10\%$.

Adsorbate chemical shifts were measured vs the pure liquids, which were used as external references. Reproducibility of chemical shifts was ± 1 Hz. The basic method for making susceptibility corrections has been outlined by Geschke (*12*) and assumes that the Wiedemann additivity rule,

$$\chi_{sys} = f_a \cdot \chi_a + f_s \cdot \chi s$$

is valid for these heterogeneous systems. Here, χ_{sys}, χ_a, and χ_s are the volume susceptibilities of the system, adsorbate and silica, respectively, and f_a and f_s are the corresponding volume fractions. The total volume of the system was determined from the adsorbent packing density, the χ_a values were taken from the tables of Emsley, Feeney, and Sutcliffe (*24*), and χ_s was calculated from the product of the packing density and the value -0.49×10^{-6} for the specific diamagnetic susceptibility of silica (*25*). The correction for the chemical shift (in ppm) was then $2\pi/3\ (\chi_a - \chi_{sys})$.

Achieving adequate signal-to-noise ratios was difficult since a monolayer of adsorbate usually corresponded to only a few microliters of liquid. This was the reason for using thin-wall tubes, for increasing the packing density of Cab-O-Sil, and for choosing adsorbates having a large number of equivalent hydrogens.

RESULTS

Line Width and Transverse Relaxation Time

It was necessary to know if resonance lines measured in the present studies were inhomogeneously broadened and, if so, if the broadening varied with the type of silica. Using the same samples, line widths and

TABLE 2

Cyclohexane Adsorbed on Silicas of Different Pore Size

Silica	Pore diameter (Å)	θ (layers)	T_2[a] (sec)	$\Delta\nu_{calc}$[b] (Hz)	$\Delta\nu_{obs}$[c] (Hz)	Relative[d] broadening	T_1[a] (sec)
Cab-O-Sil	1200	5	0.27	1.2	2.8	2.4	1.20
F-1	220	1	0.11	2.9	8.6	3.0	0.68
E-1	24	1	0.023	14	72	5.2	0.53

[a] Measured on pulse-echo spectrometer.
[b] $\Delta\nu_{calc} = (\pi T_2)^{-1}$.
[c] Measured on A-60 spectrometer.
[d] Relative broadening = $\Delta\nu_{obs}/\Delta\nu_{calc}$.

T_2 values were measured for cyclohexane adsorbed on the three silicas shown in Table 1. In Table 2 it can be seen from the ratio of T_2 to reciprocal line width (column 7) that the observed resonance lines were indeed inhomogeneously broadened. In addition, both the relative and absolute magnitude of the broadening increased with decreasing adsorbent pore diameter. Although the broadening was only about 2 Hz on Cab-O-Sil, it represents about twice the true line width. Consequently, even the narrowest line widths measured with a high-resolution spectrometer cannot be relied upon to give correct values for the transverse relaxation times of adsorbed molecules. An interesting future study would be to determine if the relative broadening also varies with adsorbate type.

The causes of the inhomogeneous broadening could arise from two sources: (a) a distribution of chemical shifts and (b) field inhomogeneity due to the particulate nature of the adsorbent. In the first case, a nonuniform adsorbent packing density could cause the adsorbate to experience a variety of chemical shift values because the chemical shift is a function of the diamagnetic susceptibility of the system which, in turn, is a function of the packing density. To test this, extreme variations in the packing density of Cab-O-Sil within a given sample tube were made intentionally and were found to cause unsymmetrical resonance lines and chemical shift changes of 1–2 Hz. However, the packing was ordinarily quite uniform, so that it should not have been a major contributor to the broadening. It is also possible, as proposed by Geschke (*12*), that an adsorbate could experience a distribution of chemical shifts on a heterogeneous silica surface known

to contain different types of hydroxyl groups. However, this seemed unlikely for cyclohexane, which is absorbed primarily by nonspecific dispersion forces.

Particle size effects were observed with the precipitated silicas. For example, the line width of benzene at monolayer coverage on silica F-1 varied with particle size range as follows: 66–88 μ, 15 Hz; 44–66 μ, 12 Hz; $< 37\ \mu$, 10 Hz. Since a constant value was not reached as the size was decreased, and no method was available for further size reduction below 37 μ, it can be assumed that there was a particle-size contribution to the line widths of these gels. An attempt was made to estimate this contribution by measuring the line widths of samples containing particles suspended in cyclohexane. The results were 2 Hz for Cab-O-Sil, 6 Hz for F-1 ($< 37\ \mu$), and 17 Hz for E-1 ($< 37\ \mu$). Unfortunately, since the line widths were very different for the two silicas of nominally similar size, and since similar broadening in suspensions of ion-exchange resins has been attributed to chemical shift (susceptibility) effects (*26*), these estimates cannot be considered reliable for correction purposes.

Effect of Adsorbent Porosity

In view of the caution that must be exercised in the interpretation of measured line widths, an experiment was designed to determine the influence of pore diameter on adsorbate line width, using the three silicas shown in Table 1. Adsorbent differences other than porosity were minimized as much as possible, but could not be totally eliminated due to differences in inhomogeneous broadening.

The line widths of cyclohexane adsorbed at monolayer coverage on the three silicas are shown in Table 2. There was a definite increase in line width with decreasing pore diameter. To further confirm the correlation, the transverse and longitudinal relaxation times were measured. They, too, indicated a greater restriction of motion in the smaller pores, so the trend established by the line-width measurements seems valid. Line-width measurements with benzene and methanol adsorbates showed the same trends found with cyclohexane.

Results with the three Davison gels fell in place with the above data, on the basis of pore volumes measured by the supplier (*27*). Davison 58 was similar to F-1, Davison 40 was similar to E-1, while Davison 81 was intermediate in pore diameter and line width.

Compression of Cab-O-Sil (in the manner used to form transparent

pellets for infrared spectroscopy) caused a marked increase in the line width of adsorbed molecules. This would be expected if one considers that such compression reduced the interparticle distance and hence reduced the pore volume. The observation that pressed pyrogenic silica behaved like microporous silica has also been reported by other workers using infrared (*28*), isotherm (*29–31*), and relaxation-time (*17*) measurements.

Effect of Surface Coverage

In the present work, the resonance positions of adsorbates on silica at monolayer coverage were found to be 40–60 Hz upfield from those of the pure liquids. The equation for the diamagnetic susceptibility correction predicts that the resonance position should move toward the liquid value as larger amounts of liquid are added to the silica. Qualitatively, the behavior of adsorbate chemical shifts with surface coverage on Cab-O-Sil followed this prediction although the observed shifts did not always correspond exactly with the calculated ones. Small deviations due to specific surface interactions will be discussed in the following paper (*11*).

However, as mentioned earlier, the behavior of line width with coverage was not as predicted. Rather, the resonance lines at high coverage were considerably broadened and often asymmetric. This was true for all adsorbates and for all medium-pore and wide-pore silicas studied. The maximum line width appeared to occur when the micropore volume had been filled, rather than at any specified number of layers (or percentages loading) of adsorbate. In addition, the broadening occurred for mixtures as well as for single adsorbates and again depended on the total amount of liquid in the pores. For example, the line width for a monolayer of cyclohexane mixed with forty layers of carbon tetrachloride was as broad as that of forty layers of cyclohexane and much broader than that of one layer of cyclohexane alone.

Karagounis originally suggested that the broadening was due to an ordering of liquid layers at high coverages (*32*). However, in view of the above-mentioned observations and those to follow, an explanation in terms of chemical shifts seems more plausible. Consider the system cyclohexane–Cab-O-Sil. At coverages below ten layers, surface diffusion in bulk liquid (*33, 34*), and the chemical shifts of molecules in different regions would be rapidly averaged. However, at higher coverages, if diffusion of liquid between the surface and macropore regions

TABLE 3

Cyclohexane Adsorbed on Cab-O-Sil at Different Coverages

θ (layers)	$\Delta\nu$[a] (Hz)	T_2[a] (sec)	Relative[a] broadening	T_1[a] (sec)
1	3.5	—[b]	—	—
5	2.8	0.27	2.4	1.20
15	3.8	0.33	4.0	1.52
40[c]	32	0.97	100	2.06
Pure liquid	—	1.73	—	1.95

[a] See Table 2.

[b] Monolayer sample was too weak to measure on pulse-echo spectrometer.

[c] Coverage corresponding to filled pore volume.

(or between particles) were slower, then individual chemical shifts would not be averaged, and one would observe the envelope of resonance lines from molecules in a continuum of environments. Line broadening of this type has been observed in studies of liquids in ion-exchange resins, where exchange of liquid molecules between particles was thought to be slow (*26*).

Further evidence for this model comes from examination of the relaxation times for the cyclohexane–Cab-O-Sil system shown in Table 3. Both T_1 and T_2 increased monotonically with coverage and approached the values for the pure liquid. The large line width at forty-layer coverage did not have a correspondingly short T_2, so it is unlikely that the width of the line was due solely to an ordering of adsorbate molecules or to the type of averaging process recently proposed by Derouane (*35*).

Attempts to vary the interparticle exchange rate by varying the temperature were inconclusive. The cyclohexane line at 10°C for $\theta = 40$ was slightly broader than at 60°, probably because the individual components were broader at the lower temperature, but no change in line shape occurred.

DISCUSSION

A possible explanation for the relation between pore size and relaxation time can be found in the chromatographic literature. Kiselev et al. (*36*), doing gas–solid chromatography of hydrocarbons on a series of silicas, found that the specific retention volumes and heats of adsorption increased with decreasing pore size. This was explained as being due to an increase in dispersion potential as pores were narrowed (*31*).

A larger dispersion potential could cause an increase in the restriction of molecular motion, thereby shortening the relaxation time.

Kiselev et al. (*36*) reported no variation of π-bond specific interaction strength with porosity. Snyder, in doing liquid–solid chromatography of aromatic hydrocarbons on silica, did note changes in specific reactivity with porosity, but he believed that these were due to changes in the geometry of surface hydroxyls rather than to pore size *per se* (*2, 37*). However, the experimental conditions were different in the two experiments; e.g., liquid chromatography is usually done near room temperature, where specific interactions may be stronger and the surface may appear more heterogeneous than at the higher temperatures normally used in gas chromatography. Specific interactions, in addition to dispersion forces, probably also contribute to relaxation times and will be considered in detail in the following paper (*11*).

The apparently general occurrence of inhomogeneous broadening means that one cannot assume that measured line widths will give reliable T_2 values. Therefore, accurate activation energies cannot be determined unless the broadening is a constant *percentage* of the line width. If the broadening is an additive constant, calculated activation energies will be smaller than the true values. This point was recently overlooked by Karagounis and Gutbrod (*38*). Line-width measurements at high surface coverages are further invalidated by the exchange broadening that occurs in that region.

The exploratory studies reported here suggest that high-resolution NMR should be useful for making relative line-width and chemical-shift measurements for low-molecular-weight molecules physically adsorbed at low surface coverages on high purity, wide-pore silicas. Future work should take advantage of narrow resonance lines by emphasizing measurement of chemical shifts and integrated intensities and by making studies with mixtures of compounds and with compounds having more than one resonance line.

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