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Review

Conformational changes and molecular dynamics of simple silica immobilized systems

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ABSTRACT

A brief review of the author's and co-workers' investigations as they relate to understanding the conformation and dynamics of chemically-modified liquid chromatographic surfaces is presented. Previously reported non-linear chromatographic behavior when using near to totally aqueous mobile phases as eluents are discussed as well as selected infrared, electron spin resonance and nuclear magnetic resonance experiments. Emphasis is placed on more recent applications of ^{2}H wide-line NMR spectroscopy and band shape analysis in infrared spectroscopy in order to study conformation and dynamics of the bonded ligands in different time regimes.

CONTENTS

1. INTRODUCTION

Since the early work carried out in the sixties [1–5], a variety of reactions have been used to chemically alter the surface of silica in order to form chromatographic packings. These procedures have ranged from simple esterifications with alcohols and silanizations with monoalkoxy- or monochlorosilanes to more complex reactions which result in oligomeric and polymeric films [6]. Following the initial modification of silica, additional synthetic steps are sometimes used in order to further alter the surface. Typically, this has been done for one of two reasons, either to eliminate residual silanols or to form more complex stationary phases. In the latter instance, a short spacer chain which contains a reactive terminal group may be grafted onto the surface. Subsequently, the attached linker-arm is used to immobilize more complex systems. The polypeptide and protein surfaces are obtained via such routes [7–17]. An important controlling parameter that is inherent to all of these processes is the underlying silica both in terms of the chemical nature of its surface and in terms of structural features in the support.

Silica is an amorphous material with a three-dimensional porous structure with several types

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of polar silanol groups at the surface [18,19]. The exact morphology of silica, in terms of the silanol groups present on the surface, is important in determining the extent and heterogeneity of the reactions used to alter its interfacial properties. The number and distribution of silanols change depending on the process employed in its production as well as the manor in which it is dried following synthesis and prior to use [19]. It is not unusual to obtain materials that are macroscopically similar (*i.e.*, in terms of the total number of groups, surface area, porosity, etc.) but that have dramatically different chromatographic properties either as unmodified adsorbents or following their chemical modification due to the microscopic heterogeneity of the surface silanols [20]. Thus, knowledge of macroscopic properties such as the number of unreacted silanol groups and percent carbon loading may provide only marginal help in ascertaining the final chromatographic performance of a bonded phase packing. To the practicing chromatographer this is a problem which manifests itself in manufacturer to manufacturer as well as batch to batch differences in column performance for a given stationary phase. As such, a tremendous amount of effort has been expended experimentally to address structural questions about the silica prior to and following chemical modification. With the advent of modern analytical techniques such as cross polarization–magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectrometry, the surface silicon atoms may be sampled directly and information about the silanols obtained [21,22]. Three resonances are typically observed from unmodified silica corresponding to the $Si(O_{0.5})_2(OH)_2$ (Q_2), $Si(O_{0.5})_3(OH)$ (Q_3), and $Si(O_{0.5})_4$ (Q_4) units. Additional information about the physical properties and chemistry of silica may be found in the texts written by Iler [23] and Unger [24].

In addition to the above structural concerns, once the silica is chemically modified questions arise in terms of distribution and conformation of the groups attached to the surface. Each of these also has received considerable attention [25–29 and refs. cited therein]. In the case of the alkyl modified silicas, which are perhaps the most widely used chromatographic materials, the earliest pictorial models proposed to explain the organization and conformation of the chains on the surface fit into two broad categories, the extended or bristle models and the collapsed or folded models. These have been reviewed previously [25–27]. Although relatively simple models were quite popular in the early to mid-seventies, they were replaced by more extensive theoretical treatments [30,31]. It is now generally recognized that the interface is conformationally complex and its organization depends on solvent conditions, temperature, pressure, chain length and structure of the attached groups, bonding chemistry, geometrical nature of the silica, etc. A summary of much of the current thinking/controversy about chemically modified packing appears in this volume of the *Journal of Chromatography*.

In characterizing/understanding the interfacial properties of bonded phases in terms of the organization of the attached groups on the surface, it is important to examine how organization is influenced by the experimental and structural properties of the bonded groups such as chain length and functionality as well as constraints such as temperature [20,25,32–36], solvent composition [37,38], etc. For example, in one solvent bonded linear alkyl groups may be found as clusters or may be more solvated under other conditions, whereas, bonded chains which contain polar functional groups may interact strongly with unreacted surface silanols or polar components of the eluent. Similarly, it is important to evaluate how the attached groups and underlying surface can influence the composition and structure of the intercalated solvent [37–39]. Under one set of reversed-phase conditions such as when binary mixtures of methanol and water are used as the eluent, the surface phase composition may be similar to the bulk mobile phase composition, whereas with other aqueous–organic solvent combinations the bulk and intercalated mobile phase compositions may differ dramatically [37,38]. The surface phase composition as a function of the volume fraction of water–methanol and water–acetonitrile mobile phases on octyl and octadecyl columns has been reported recently to illustrate this effect [38].

The idea of preferential solvation/extraction of one of the mobile phase components is a concept which was established in the seventies [40–45] and later discussed theoretically in terms of a *breathing* surface model [30]. In this later theoretical treatment, the dimensionality of the bonded layer was pictured to change depending on the mobile phase composition. Several approaches have been used in order to ascertain information about the layer dimensions including neutron scattering experiments [46–47]. Thicknesses of 10 ± 2 Å and 17 ± 2 Å have been reported respectively for C_8 and C_{18} under the hydro–organic conditions studied. More recently, an extended treatment which deals with the molecular mechanisms involved in solute retention under hydro–organic liquid chromatographic conditions has been published [31]. These considerations are complicated further by the dynamic nature of the system (*i.e.*, immobilized flexible chains) and uncertainties introduced based on time.

For about a decade investigators have been attempting to address important questions concerning chemically modified chromatographic surfaces in terms of their time dependent nature (*i.e.*, the molecular dynamics present and their influence on the resulting interface). This aspect is not only important in understanding the surface but also in knowing how information derived from different types of experimental techniques relate to each other. For example, it has become quite popular to study the properties of alkyl and related bonded phases (*e.g.*, amino, cyano, phenyl, etc.) using a variety of spectroscopic methods such as NMR, electron spin resonance (ESR), infrared (IR), luminescence, and a host of other techniques. Although these approaches are used to examine time independent information (*i.e.*, assuming chemical stability of the system) such as chemical composition and structure, in many instances, time dependent information also is obtained such as that contained in the band shapes as well as life times and relaxation rates.

Since the various spectral approaches cover a broad frequency range, they sample different processes and time regimes. Thus, events which appear stationary in one time scale may be quite dynamic in another time regime. This leads to questions of temporal/spatial uncertainty if a given model is based around a single type of measurement (*i.e.*, information obtained in a single time scale). A slightly different way of posing this same question is to consider time dependent information obtained via infrared techniques which sample processes that are in the pico to sub-picosecond scale with information obtained via nuclear magnetic resonance techniques (*e.g.*, wide-line ^{2}H experiments) which are sensitive to motions in the micro- to nanosecond range. Thus, the alkyl chains immobilized to silica, which are heterogeneously distributed on the surface, undergo various vibrational, rotational and translational fluctuates. These processes occur at different rates. For example, the various equilibrium conformations of silica-immobilized chains can be frozen in time when viewed by IR spectroscopy [48–51] whereas when they are examined by NMR spectroscopy they are conformationally dynamic [52–54]. In some cases even within a technique the immobilized chains may be conformationally flexible at one end and restricted at the other end [53]. Each of these are discussed in greater detail in section 3.

A final and important consideration about the uncertainty of experimental information/approaches comes when comparing data obtained from direct type measurements, which sample the system, itself (*e.g.*, IR or NMR techniques), with data obtained using a probe molecule to sample the system such as chromatography (*i.e.*, the solute molecule) or luminescence (*i.e.*, a dye molecule) experiments. This same question can be asked in slightly different terms. How does the dimensionality of the probe perturb the system/measurement? In many cases the molecular probe may be as large or in some instances larger than the chains being sampled. Two examples of this are the use of large polynuclear aromatic compounds as chromatographic solutes and the use of large dye molecules to carry out phosphorescence measurements. Although the probe molecule may be considered to be infinitely dilute at the macroscopic level, the presence of the probe at the site being sampled may be in contact with only a few of the surface anchored groups. This presents an interesting paradox for non-rigid–dynamic systems: If the solute or dye is large compared to the chains it is interacting with, at the time of interaction are the chains the same as when the probe molecule is absent or being studied by a less perturbing smaller solute molecule or by a non-invasive technique such as NMR spectroscopy? Thus, the various experimental techniques often provide different information about the system which may or may not be the same and models that are based on a single type of measurement at best are uncertain and may be experimentally biased towards a given set of conditions.

For over twenty years the author and coworkers have used a variety of chromatographic, spectrometric, thermal and other methods (Fig. 1) to carry out either direct measurements on the attached groups or underlying surface (*i.e.*, nuclear magnetic resonance and infrared spectrometry) or indirect measurements using probe molecules to sample the interfacial region of bonded siloxanes such as inverse chromatographic experiments or immobilized probe molecules which contain spectrometrically active centers such as a cyano group or nitroxide radical in combination with infrared or electron spin resonance experiments. A few representative examples of various types of data obtained from the author's work are shown in Figs. 1–8. Thus, the remainder of the current manuscript will present a brief review of this work in an attempt to develop/postulate a pictorial model of simple chemically modified systems such as alkyl and ω-alkyl phases based on the conformational and dynamic ideas discussed above.

2. CHROMATOGRAPHIC STUDIES

The use of chromatography in order to obtain physicochemical information about a material is well established and has been used since the fifties. With experimental care and appropriate corrections, a solute's retention volume at a given temperature and as a function of temperature can be used to evaluate respectively the changes in free energy and in enthalpy associated with its surface interactions. As such, numerous chromatographic experiments have been carried out in order to examine a host of materials including silica as well as when silica has been modified with various inorganic salts, liquid phases and via chemical derivatization.

Under well behaved conditions, where the separation mechanism is constant, a linear relationship is obtained from a plot of ln V_s *vs.* $1/T$ where V_s is the corrected specific retention volume and T is the column temperature in K. Under other conditions non-linear behavior may be observed due to system heterogeneity as well as changes in organization of the system. These latter types of measurements are especially interesting in attempting to understand chemically modified liquid chromatographic surfaces and to develop pictorial descriptions of the separations mechanisms involved under various eluent conditions.

One type of non-linear experiment developed in the author's laboratory about fifteen years ago [32] involves the measurement of changes in solute retention as a function of temperature under high to totally aqueous eluent conditions. When alkyl and related modified silicas are initially treated with an organic solvent such as methanol or acetonitrile and then the mobile phase switched to water the immobilized chains are believed to form aggregate subunits. Often, these subunits contain entrapped solvent which is released over hundreds of column volumes. The degree of entrapment and kinetics of release have been related to the size, shape and polarity of the solvent [55]. For example, a linear alcohol with a longer hydrophobic tail such as 1-butanol has been shown to be released slower than a smaller alcohol such as methanol. Of the solvents examined, acetonitrile was found to effect the aggregated state least. Thus, it has been used as the conditioning solvent in work which is discussed below.

Once the surface is conditioned with an organic solvent such as acetonitrile and then water used as the eluent, as the surface is heated, a point is reached where it wets (*i.e.*, the immobilized chains can reorder/resolvate). This phenomenon was first observed for silica modified with alkyl chains of intermediate length, C_8–C_{10} [32]. Based on these initial findings an aggregation/

deaggregation model was postulated in order to explain wetting (*i.e.*, reordering/resolvation) of the immobilized chains. The idea of interfacial aggregation also has been suggested by others in terms of a microscopic *micro-droplet* model [56] and is consistent with other aggregation phenomena which is observed under reduced wetting conditions such as micelle and bilayer formation.

Shown in Fig. 1 is a representative plot of the non-linear behavior expected when a solute is chromatographed under reordering/resolvation conditions. The curves labelled i represent the initially observed change in retention after the column is first conditioned with an organic modifier and water used as the eluent. This initial thermal curve contains two distinctly different regions, a linear portion which is the more typically expected behavior and a non-linear portion which falls between the points labelled T_0 and T_f and which indicates a significant change in the separation mechanism controlling solute retention. These two points correspond respectively to the initial and final surface reordering/resolvation temperatures. Following this initial thermal behavior (curves i), when the column is cooled and a new set of retention *vs* temperature data collected they are fitted by a single linear relationship, lines r in Fig. 1. Additional cooling and heating curves all fall on curves r. However, the surface can be converted to its original state via treatment with an organic solvent such as acetonitrile and then water. Similar cycling/hysteresis effects have been observed in numerous other experiments carried out under equivalent low wetting conditions and can be rationalized on the basis of a two-state model where curves i result from an aggregated surface state and curves r from a wetted/extended surface state.

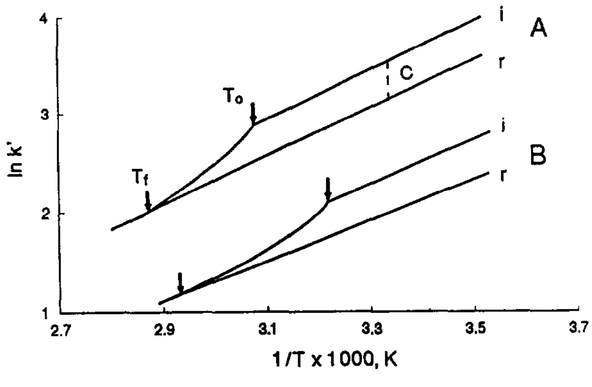

Fig. 1. Representative plot obtained from a non-linear reordering/resolvation experiment using water as the eluent [see refs. 20 and 32–36]. Curves A and B represent silicas with differ silanol heterogeneity. Evaluation cycle: (i) initial run following pretreatment of surface with an organic solvent and (r) re-evaluation after reaching T_f and cooling of column. Dashed line (c): difference in k' for a solute before and after surface reordering/resolvation.

The difference between the initial curves i and the curves obtained after reordering/resolvation has occurred (curves r) is represented in Fig. 1 by the dashed line labelled C. The magnitude of C can be related to the surface coverage of the immobilized alkyl groups within a certain critical range which falls between normalized carbon values of approximately 1–1.5 for bonded intermediate chain length hydrocarbons [32]. Interestingly, in independent NMR studies significant changes in ^{13}C relaxation measurements have been correlated with the same level of coverage needed in order to observe the reordering/resolvation phenomenon [57] and has been explained in terms of increased chain-chain interaction at these coverages.

The magnitude of C in Fig. 1 also can be related to the structure of the solute [32,36]. Shown in Fig. 2 are plots of ln k' *vs.* carbon number for two homologous series of solutes, linear alcohols (triangles) and *p*-alkylphenols (circles). These data have been redrawn from a previous study [36] and represent values before (filled) and after (unfilled) thermal treatment of the surface. In both cases the slopes of the two sets of lines, which are related to the incremental methylene selectivity, are statistically parallel for the two solute classes before and after the surface has undergone resolvation. However, the difference between retention before and after reordering/resolvation was about 30% for the phenolic solutes compared to only 8% for the linear alcohols. It also was noted in this same study [36], as well as other related studies, that as the solute is more rigid/sterically hindered that the difference between curves i and r increase (*i.e.* shown respectively as filled and unfilled data points in Fig. 2). Likewise, the presence of an increased number of polar sub-

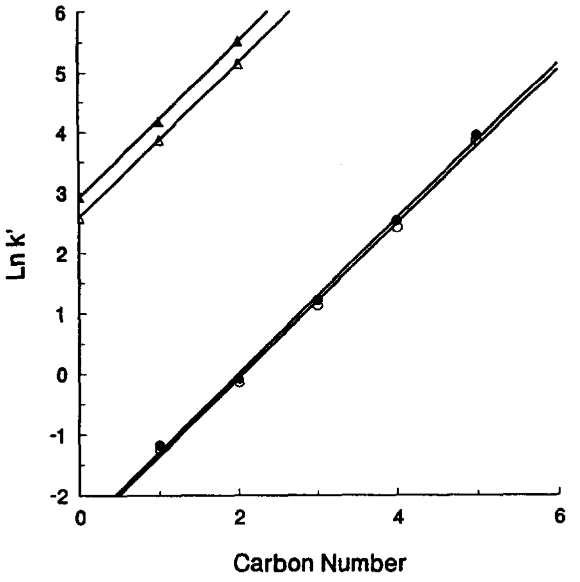

Fig. 2. Plot of ln k' *vs.* carbon number, showing incremental methylene selectivity. ○, ● = linear alcohols as solutes; △, ▲ = *p*-alkylphenols as solutes; ●, ▲ = initial run following treatment with an organic solvent, ○, △ = obtained after surface reordering/resolvation.

stituents in the solute also enhances this difference [36]. Thus, changes in retention before and after surface reordering/resolvation, C, can be correlated to structural features in the solute such as size, shape, rigidity and substitution.

In addition to the above considerations, the total temperature range ($T_f - T_0$) over which thermally induced reordering/resolvation occurs can be correlated to the silica used to prepare the bonded phases [20]. This also is illustrated in Fig. 1 for two different types of materials which are labelled A and B. Although both materials are heterogeneous in terms of their silanol distributions, curve A represents a material which is microscopically less heterogeneous as illustrated by the narrower range over which reordering/resolvation occurs (*i.e.*, smaller value of $T_f - T_0$). Recently, this procedure has been used to characterize the heterogeneity of five different chromatographic grade silicas. For the samples studied, Zorbax Sil material was found to have the smaller difference between T_f and T_0 [20] which appears to be consistent with its reported enhanced chromatographic performance. In this same study differences in pore size for similarly manufactured materials did not significantly effect T_0. For example, LiChrosorb Si-60 and Si-100 porous silica had average reported values of 44.7 ± 0.7 and 44.6 ± 0.7 respectively.

In other studies, values of T_0 have been determined for a number of different polar and non-polar phases [32–34] and as a function of bonding chemistry [35]. Linear correlations have been observed between carbon number of the anchored groups for a particular homologous series of bonded phases. This is illustrated in Fig. 3 for alkyl (d), chloroalkyl (c), bromoalkyl (b) and cyanoalkyl (a) modified silica. Interestingly, these linear relationships are nearly parallel and are off-set to higher temperatures for a given hydrocarbon chain depending on the terminal substituent present in the phase. The observed order for the three groups shown in Fig. 3 is chloro < bromo < cyano (curves c, b and a). The contribution of several other functional groups also were examined through single point measurements [34].

Based on the above results a three term model was proposed to explain variations in reordering/resolvation temperature in terms of the chain–chain interactions between the bonded groups, hydrophobic interactions between the bonded chains and the aqueous mobile phase and specific interactions between the solvent, bonded chains, and surface silanols. Further, it has been suggested that solvent surface interactions stabilize the reorganized extended state following thermal treatment. Enhanced solvent structuring at the

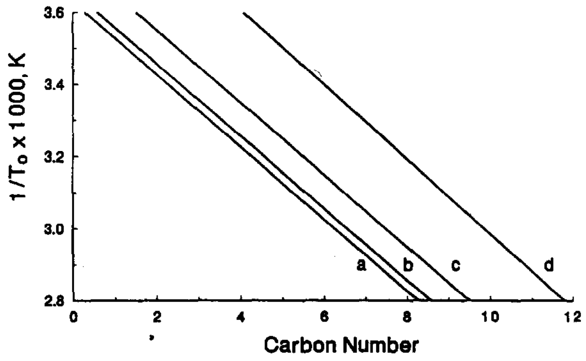

Fig. 3. T_0 *vs.* carbon number for different bonded homologues. Ligand type: (a) cyanoalkanes, (b) bromoalkanes, (c) chloroalkanes, (d) alkanes.

surface of alkyl modified silica in contact with other polar solvents also has been observed via NMR measurements of relaxation as a function of solvent viscosity [39] and temperature [58].

However, T_0 has been found to be constant for a given immobilized ligand irrespective of whether it is attached via a mono, di, or trireactive silane [35] assuming the surface reactions are carried out under conditions where bulk polymer phases do not develop. This latter observation supports the idea that bonding occurs in microscopically heterogenous patches which is controlled via the underlying surface structure. Further the internal organization of these patches more nearly resemble that of microscopic liquid droplets than ordered systems. Similar ideas are supported by the work of others [*e.g.*, ref. 56]. Recently, evidence of liquid-like behavior has been observed from distinct features observed in low temperature ^{2}H NMR quadrupole splitting experiments (*i.e.*, see Fig. 7 and the related discussion presented in the text). However, under certain conditions more ordered systems can be obtained. The degree of order/disorder is system dependent and is influenced in a complex way by a large number of variable both during the synthesis of the materials as well as their experimental use.

3. SPECTROMETRIC STUDIES

Shown in Fig. 4 are partial infrared spectra which cover the nitrile stretch region for 3-cyanopropyl-modified silica solvated by a non-polar solvent, hexane (a) and by a polar solvent, 1-butanol (c) [49]. Also included for comparative purposes are solution spectra for 3-cyanopropyltrimethylsilane (CPTMS) dissolved in hexane (b) and in 1-butanol (d). The complex band for the bonded cyanoalkyl groups in contact with hexane results from a combination of an infrared band (*i.e.*, broader and centered at higher wavenumber) which arises from groups that hydrogen bond with free silanols on the silica and an infrared band (*i.e.*, narrower and centered at lower wavenumber) for nitrile groups which are sterically hindered and cannot interact with the surface. In the presence of 1-butanol, a hydrogen bonding solvent, a single broadened band (*i.e.*, similar in shape to the solution spectrum of CPTMS, d) is obtained as the result of the strong interaction of the alcohol with the surface silanols and the resulting displacement of the bonded cyanoalkyl groups from the surface. When similar studies were carried out on silica modified with other longer chain length cyanoalkyl ligands analogous results were obtained. Likewise, the dry state spectra of these same materials also contain a complex band for the nitrile stretch with the relative ratio of the hydrogen bonding to free groups decreasing with increasing temperature as expected thermodynamically [50].

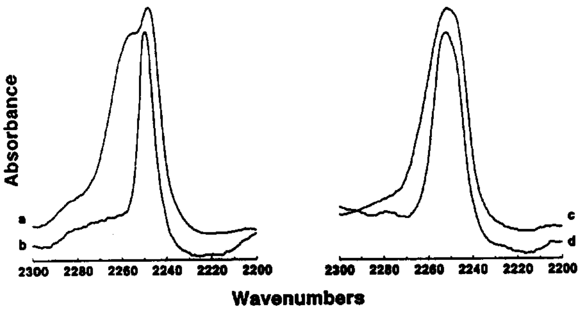

Fig. 4. Infrared spectra of the nitrile stretch region for silica chemically modified with 3-cyanopropyl groups (spectra a and c) and free 3-cyanopropyltrimethylsilane (spectra b and d). Solvents: (a and b) hexane; (c and d) 1-butanol.

As in the case of the previously discussed chromatographic results, the above IR data also are consistent with a heterogeneous patch-type reaction model. Groups that bond within a rich area or cluster are sterically hindered by neighboring groups from interacting with free silanols, whereas, groups at the edges of such clusters or groups which are attached in isolated areas can form hydrogen bonds with the surface in the dry state and under non-displacing solvents such as hexane. This same heterogeneous patch/displacement model has been observed for bonded cyanoalkyl phases via chromatographic and IR partial displacement measurements [51] and NMR relaxation and line shape measurements [59] as well as for other anchored systems by electron spin resonance studies using immobilized 2,2,6,6-tetramethylpiperidiene oxide (TEMPOL) [60] and by recently measured changes in low temperature ^{2}H NMR line shapes (Fig. 7) [61].

Although ESR in conjunction with spin probes such as TEMPOL has been employed for many years to study various bulk polymers, biological membranes and thicker grafted surface films [62–66], its use as a means of examining high-performance liquid chromatographic bonded phases had not been reported prior to the author's initial studies [60]. The spin Hamiltonian for the nitroxide radical is

$$H = g\beta H_0 S + AIS + g_N \beta_N H_0 I \qquad (1)$$

where $I = {}^{14}$N nuclear spin, β = Bohr magneton, g = Lande factor, H_0 = magnetic field strength, and S = electron spin value. The first term in eqn. 1 is the electron Zeeman term. A in the second term arises from the hyperfine interaction between the magnetic moments of the nitrogen nucleus and the free electron. Both g and A are axial with nearly the same principal axes. The last term is the nuclear Zeeman term. For isotropic systems where the spin labels tumble rapidly enough to completely average the hyperfine and Zeeman interactions, A_{iso} is $1/3(A_{xx} + A_{yy} + A_{zz})$ and g_{iso} is $1/3(g_{xx} + g_{yy} + g_{zz})$. A_{zz} is the component of the hyperfine coupling tensor perpendicular to the N–O plane and is half of the low- and high-field extremes in the rigid-limit spectrum. It is sensitivity to the polarity of the local environment. In general A_{zz} increases with increases in the solvent's dielectric constant and is especially sensitive to hydrogen bonding of the N–O group [67,68].

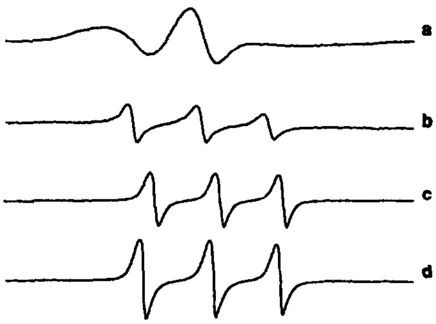

Fig. 5. Electron spin resonance for silica chemically modified with TEMPOL (spectra a and b) and free TEMPOL (spectra c and d). Solvents: (a and c) hexane; (b and d) 1-butanol.

Shown in Fig. 5 are representative ESR spectra for TEMPOL modified silica in the presence of hexane and 1-butanol [60]. Spectrum a indicates that the nitroxide group is motionally restricted and is in a polar environment. This would arise only if the bonded TEMPOL ring, which is anchored to the surface via a four bond spacer unit, is conformationally rotated into the plane of the surface and the nitroxide radical is in close proximity to a surface silanol. In 1-butanol the spectral shape indicates the presence of a less polar environment with greater ring mobility which would result via displace of the TEMPOL molecules from the surface. These surface state results are opposite from what is normally observed based on polarity arguments of the solvent alone [67,68] (*i.e.*, free solution of TEMPOL dissolved in either hexane or butanol) as shown in Fig. 5, spectra c and d. Thus, the ESR data, as in the case of the IR studies, can be rationalized in terms of a major conformational change in the immobilized TEMPOL molecule as the result of solvents such as 1-butanol which interact strongly with the unreacted surface silanols [60].

A variety of other spectrometric experiments have been carried out in order to study silica and chemically modified by the author and co-workers as well as by numerous other investigators. These have ranged from conventional solution [39,57,58,69–71] to solid-state cross-polarization magic angle spinning [21,22,71–78] to ^{2}H quadrupole splitting [61,79,80] measurements. More recently we not only have been interested in the conformational aspects of bonded phases but in the time dependent motional fluctuation which occur at the interface in both the intermediate [53,54,61] and fast time regimes [52,61]. Each of these topics are considered below.

Although the dynamic nature of semirigid systems such as macromolecules [81,82], membranes [83–86] and liquid crystals [87,88] has been studied often by wide-line ^{2}H NMR techniques, the investigation of chemically modified silica by ^{2}H NMR methods has been limited [53,54,61,79,80] especially chromatographic phases [53,54,61]. The theory to describe the motional and conformational aspects of silica immobilized alkyl chains is similar to that used for polymer, liquid crystal and lipid bilayer systems [89–91]. In the absence of motion, the rigid limit condition, a C–^{2}H bond, which is oriented at an angle θ with respect to an external magnetic field, produces a doublet with a splitting [92] $\Delta\nu$:

$$\Delta\nu = 3/4Q_0(3\cos^2\theta - 1) \qquad (2)$$

where Q_0 is the static quadrupole coupling constant.

For polycrystalline samples in which all orientations of the C–^{2}H bond are equally probable, a uniaxial powder pattern is obtained with peak separation of 123 kHz and base width of 246 kHz (see refs. 53 and 92 for a simulated spectrum using a Q_0 of 165 kHz and a natural line width of 0.25 kHz). In some cases the parallel components are not distinguishable due to noise and natural line broadening [89].

In cases other than the rigid limit, motional components alter the resultant line shape. In the simplest case where rapid fluctuations of the carbon–deuterium bond occurs about a well-defined arbitrary axis which is orientated at an angle α, a uniaxial power pattern is obtained with a reduced quadrupole splitting defined by eqn. 3.

$$\Delta\nu = 3/4Q_0[1/2(3\cos^2\alpha - 1)] \qquad (3)$$

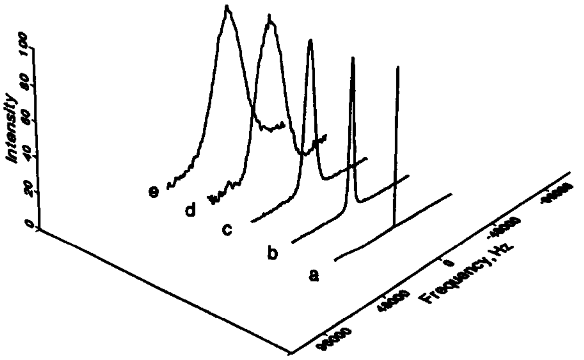

Fig. 6. ^{2}H NMR spectra for physically coated and chemically modified surfaces at ambient temperature. Spectra: (a) silica physically coated $(CH_3)_3Si(CH_2)_3C^2H_2(CH_2)_5CH_3$, (b) silica chemically modified with $Cl(CH_3)_2Si(CH_2)_{11}C^2H_3$, (c) silica chemically modified with $Cl(CH_3)_2Si(CH_2)_{10}C^2H_2CH_3$, (d) silica chemically modified with $Cl(CH_3)_2Si(CH_2)_3C^2H_2(CH_2)_5CH_3$, and (e) silica chemically modified with $Cl(CH_3)_2SiC^2H_2(CH_2)_5CH_3$.

Recently, we have used ^{2}H NMR techniques to examine the motional dynamics of specifically deuterated alkyl groups chemically anchored to silica in the dry state [53] and when the materials were in contact with different solvents [54,61]. These labeled materials were prepared with LiChrosorb SI-60 under similar conditions used to synthesize other chromatographic phases. The exact experimental details and other related information are found in the cited references. Representative spectra from this work are illustrated in Figs. 6 and 7. Shown in Fig. 6a is liquid-like behavior (*i.e.*, a narrow isotropic line) obtained for a physically coated sample. This spectrum is due to complete averaging of the quadrupole interactions. However, the line widths for the chemically modified surfaces were broader and ranged from 6.5 to 46 kHz depending on the position of labelling (Fig. 6b–e). The reduced line widths of 6.5 and 16 kHz for the terminal methyl (Fig. 6b) and adjacent methylene (Fig. 6c) deuterons, respectively, indicate that partial averaging of the quadrupole interactions occur via 2–3 bond rotations. The nearly identical (46 and 40 kHz, respectively) line widths for the surface bound and the forth position deuterated carbons is within experimental error to the calculated value (*i.e.*, 44 kHz) for averaging via single rotational process. These data thus suggest that on the NMR time scale there are at least two different motional domains along the chains. Near the surface and in the chain interior regions, the bonded groups are

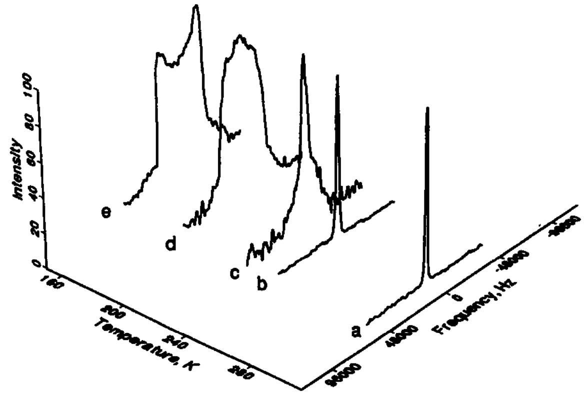

Fig. 7. ^{2}H NMR spectra for [12-^{2}H]dodecyl-modified silica in contact with dodecane. Spectra: (a) 298 K, (b) 243 K, (c) 223 K, (d) 183 K, (e) 143 K.

translationally/conformationally restricted on the deuterium time scale and at the unbound end the chains are more dynamic and less correlated.

Similar ^{2}H NMR studies have been carried out in order to examine the dynamics of alkyl-modified silica in the presence of surfactant and mesogenic molecules [54] as well as aqueous and non-aqueous solvents [54,61]. Deuterium spectra of ([12-^{2}H]dodecyl)dimethyl-modified silica in contact with dodecane are shown in Fig. 7 as a function of decreasing temperature. In this latter work again materials were prepared using LiChrosorb SI-60 at a level of coverage of 8.6% based on elemental carbon analysis. Spectra a and b are isotropic solution spectra. The slight increase in the peak width as a function of decreasing temperature is due to increased viscosity of the solution. At lower temperatures increased broadening and unique changes in line shape occur (spectra c–e). The latter spectral changes reflect freezing of the sample initially into an amorphous solid (spectra c and d) and, later at lower temperatures, a solid–solid transition from an amorphous state to a more ordered crystalline-like state (*i.e.* the unique Pake pattern can clearly be seen in the 143 K spectrum). Similar results have been reported for solid–solid transitions in linear hydrocarbons [93]. However, the temperature where the bonded ligands/interface undergo these changes is depressed from the pure solution state..

The above NMR results demonstrate the complexity of the interface and its ability to undergo conformational transitions which are induced by the contact solid and temperature. Likewise, they show differences in the on-set of the solid state changes, which likely is related to the heterogeneous nature of complex system formed between the bonded dodecyl chains and the contact solvent, dodecane. Interestingly, the unique changes in line shape also suggest that the chains behave more like disordered liquids even when they are in contact with very similar solvents such as dodecane and that crystalline-like behavior is observed only at very low temperatures. Since the above study was carried out on materials with intermediate coverage it is difficult to extrapolate these data to higher coverage materials. However, the above techniques should provide a means of experimentally evaluating theoretically predicted ordering behavior for dense phases which has been suggested by others [31]. These ^{2}H NMR studies are now in progress as well as work to examine the influence of more polar solvents on phase organization. Additionally, more extensive details of the low temperature solid-state behavior of alkyl phases in contact with several other hydrocarbon solvents will be discussed in greater detail in a forthcoming manuscript.

Most recently we have been interested in examining the fast time regime motional dynamics for two types of chemically modified surfaces (*e.g.*, alkyl and cyanoalkyl modified materials) [52]. This is possible by placing emphasis on the time evolution of the vibrational Hamiltonian in the Heisenberg representation as originally discussed in the papers of Gordon [94–97] and later expanded by Rothchild [98–100] to larger molecules including order/disorder, thermal fluctuations and heterogeneity in mesogenic systems. Using these techniques molecular dynamics in the pico- and sub-picosecond time regimes may be studied.

The correlation function which is a statistical representation of the fluctuations of the orientation and amplitude of vibrational transition moment can be obtained from the Fourier transform of an infrared absorption band. Thus, the correlation function,

$$C(t) = \int \kappa(\omega) \exp[i(\omega - \omega_0)t] \, d\omega \qquad (4)$$

where the quantity $\kappa(\omega)$ is the normalized absorption at a given angular frequency ω centered about the angular frequency ω_0.

Until recently most work with the vibrational-rotational correlation function (VRCF) was with small symmetric molecules in either the gas or liquid phases as well as with molecules dissolved in solution [101,102]. Even in the simplest cases theoretical interpretation of the VRCF can pose a formidable problem due to intramolecular vibrational coupling, resonance interactions and molecular collisions [103,104]. Nevertheless, we have attempted to use the VRCF in order to obtain phenomenological information on two anchored systems, alkyl and cyanoalkyl groups, which represent chromatographically important phases [52,61]. This was the first reported application of the VRCF to study such systems. Shown in Fig. 8 are representative VRCF curves for the non-hydrogen bonding CN band from (2-cyanoalkyl)dimethylsilyl groups immobilized to silica (curves a–c) and the C^2H_3 band from [12-^{2}H](dodecyl)dimethylsilyl groups immobilized to silica (curves d–f) as a function of temperature. Also, shown in Fig. 8g for reference purposes is the VRCF curve for carbon monoxide dissolved in chloroform. Clearly the curves for the anchored system decay at a slower rate than the less hindered solution curve for carbon monoxide. Further, in a general sense the decay of the correlation functions for the surface-immobilized systems are made up of a shorter time region of negative curvature and a longer time region that is approximately exponential. Additionally, plots of the negative natural logarithm of the correlation function can be linearly related to temperature. However, over an extended range such plots for the longer dodecyl phase show biphasic behavior which can be correlated with similar trends measured spectrometrically, chromatographically, and calorimetrically. Further, it would appear that this behavior is related to thermally induced conformational changes in the bonded alkyl chains. Thus, our preliminary results [52] would seem to demonstrate the potential use of the VRCF to study fast regime motional dynamics for chromatographic and related semirigid systems.

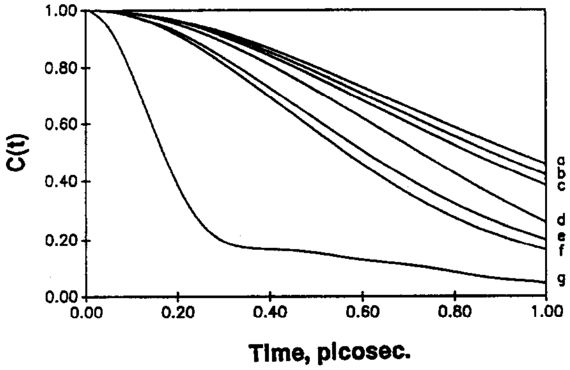

Fig. 8. VRCF curves for chemically modified surfaces for a time evolution of 1 ps. Curves: (a–c) CN band from 2-cyanoethyl-modified silica for respective temperatures of 403, 473 and 510 K, (d–f) C^2H_3 band from [12-^{2}H]dodecyl-modified silica at respective temperatures of 298, 343 and 433 K, (g) CO dissolved in chloroform at ambient temperature.

4. CONCLUSIONS

The current manuscript presents a brief overview of the author's and co-workers' efforts to experimentally study the complex nature of chemically modified silica and their use as chromatographic phases. Data from the various experimental approaches reviewed above appear to be self-consistent and indicate that the interfacial properties of the surfaces used as chromatographic phases are complex and variable. However, it would appear that in many cases the heterogeneous nature of silica leads to phases which are made up of regions of organically rich areas and areas which contain fewer bonded groups than uniform distributions of the groups. The exact nature of the surface patches (*e.g.*, size and number) varies depending on the surface and structural properties of the silica as well as with properties of the bonded groups such as their size, shape and degree of coverage.

Depending on the solvent conditions at the interface it may be either: (1) more liquid-like in terms of reduced conformational order and increased conformational/transnational dynamics or (2) more rigid with either micro-liquid-like organization or more self-organized. The organization and dynamics of the immobilized groups are influenced by many system and experimental variables. Thus, at any instance in time, depending on conditions present and the structural features of the surface and the attached groups, the interface many be conformationally and dynamically different. This is further complicated by the fact that different measurements/experiments sample events under a certain set of conditions and time constraints. Some provide average properties of the event such as a chromatographic retention, some may sample various conformations such as an infrared measurement, and yet others may provide a combination of both. Thus, caution should be exercised when developing ideas and models based on a single set of measurements.

It is clear that even the most developed mathematical models, which may provide useful macroscopic descriptions of the interface, cannot describe adequately the exact/detailed microscopic features of the surface. Nevertheless, many of the current macroscopic models are quite useful in predicting chromatographic behavior and thus serve as an aid in methods development.

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