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Vibrational Spectroscopy of Chromatographic Interfaces

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1. Structure-Function Studies in RPLC Stationary Phases

Chromatographic separations play a central role in DOE-supported fundamental research related to energy, biological systems, the environment, and nuclear science. The overall portfolio of research activities in the Separations and Analysis Program within the DOE Office of Basic Energy Sciences includes support for activities designed to develop a molecular-level understanding of the chemical processes that underlie separations for both large-scale and analytical-scale purposes. The research effort funded by this grant award was a continuation of DOE-supported research to develop vibrational spectroscopic methods to characterize the interfacial details of separations processes at a molecular level.

A. Raman Spectroscopy of Alkylsilane-Based RPLC Stationary Phase Materials

Studies of stationary and mobile phase structure in this laboratory seek a unified molecular picture of stationary phase-stationary phase, solute-stationary phase, solute-mobile phase solvent, stationary phase-mobile phase solvent, and mobile phase solvent-solvent interactions that dictate retention in reversed phase liquid chromatography (RPLC.) In order to utilize Raman spectroscopy for elucidation of structural parameters for RPLC stationary phases (SPs) that are relevant to retention mechanism, model systems must be identified and validated in terms of spectral indicators of the structural attribute that one wishes to understand. Toward this end, by analogy with our earlier work in identifying Raman

spectral indicators of conformational order for hydrogenated alkyl chain systems [11]ⁱ, conformational order indicators for perdeuterated alkyl chain systems were identified in the Raman spectra of nonadecane-*d*₄₀, polyethylene-*d*₄ and stearic acid-*d*₃₅ [20]. Six spectral indicators of conformational order in the perdeuterated systems were identified: $I[\nu_a(\text{CD}_2)_{2196}]/I[\nu_a(\text{CD}_2)_{2172}]$, $I[\nu(\text{C-C})_G]/I[\nu(\text{C-C})_T]$, $I[\nu_s(\text{CD}_3)]/I[\nu_a(\text{CD}_2)_{2172}]$, $I[\nu_s(\text{CD}_2)]/I[\nu_a(\text{CD}_2)_{2172}]$, and the full-width-at-half-maximum (FWHM) and frequency of the $\nu_s(\text{CD}_2)$ mode. Among these indicators, the intensity ratio $I[\nu_a(\text{CD}_2)_{2196}]/I[\nu_a(\text{CD}_2)_{2172}]$ is considered a primary indicator of conformational order, since it responds to alkyl chain conformational changes in a manner similar to the primary $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ indicator for hydrogenated systems. Other indicators were also correlated to this primary indicator to derive a better understanding of the effect of structural attributes on conformational order in perdeuterated alkyl chain systems.

Considerable past efforts funded by this award focused on elucidating structure-function relationships in SPs based on octadecylsilane bonded layers.[4,5,7,8,12-15] The majority of the past efforts were spent studying a series of high-density octadecylsilane stationary phase materials prepared on YMC 3- μm silica particles by Dr. Lane C. Sander at NIST.[12-15] These materials were prepared using either “surface polymerization” or “solution polymerization” approaches for attaching the octadecylsilane to the silica, and had very high octadecylsilane surface coverage ranging from 3.1 to 6.5 $\mu\text{mol}/\text{m}^2$ (conventional octadecylsilane phases are in the 2 to 3 $\mu\text{mol}/\text{m}^2$ range.) Previous work by Dr. Sander and coworkers had shown these phases to exhibit unique shape selectivity for certain polynuclear aromatic hydrocarbon (PAH) solutes. This series of phases was extremely useful in better understanding the potential utility of Raman spectroscopy for elucidating fundamental molecular information about interfacial processes in RPLC, since the 6.5 $\mu\text{mol}/\text{m}^2$ material is essentially a full monolayer coverage “standard” phase (estimated maximum coverage based on reactive silanol density is known to be $\sim 8 \mu\text{mol}/\text{m}^2$) to which the spectral response of the others could be compared. Using these materials, extensive studies of the Raman spectral response in air and in fourteen different solvents as a function of temperature were performed.

In new work during this grant award, the effects of electrolyte, acidic and basic compounds, and pH on the conformational order of two of these high-density octadecylsilane SPs was determined.[16] Both phases demonstrated an increase in conformational order in 5 to 200 mM aqueous electrolyte solutions relative to water. These observations were interpreted in terms of “salting-out” of these phases in aqueous electrolyte solutions, thereby causing alkyl chain intermolecular interactions to increase with a concomitant increase alkyl chain order. Although the presence of acidic and basic compounds generally has no effect on the conformational order of either stationary phase as a function of pH, the higher

ⁱ Numbers in brackets [] refer to citations included in publication list at the end of this report.

coverage stationary phase exhibited pH-dependent changes in aqueous solutions of benzoic acid. At pH values below the benzoic acid pK_a , the conformational order of this stationary phase was unchanged relative to that observed in the same pH solution in the absence of benzoic acid. In light of independent evidence that such monosubstituted aromatics interact with the octadecylsilane stationary phase under these conditions, the absence of a measurable effect on alkyl chain order for these conditions was attributed to benzoic acid self-association at the stationary phase-mobile phase interface. In contrast, at pH values above the pK_a of benzoic acid, slight disordering of the alkyl chains was observed and is attributed to repulsive interactions between retained benzoate anions. These results have relevance for both RPLC and capillary electrochromatography that utilize such phases and represent the first report of the structural consequences of electrolytes and changes in pH of aqueous mobile phases.

The effect of pressure in solvent environments on the conformational order of two commercially-available octadecylsilane stationary phase materials, one monomeric and one polymeric, in chloroform, benzene, acetonitrile and water were investigated.[19] Differences in conformational order were quantified before and after exposure to pressurized solvent environments, and changes compared to effects of solvation relative to air in the same four solvents. Minor effects (<2-3% change in order) due to pressure were noted for the monomeric stationary phase in all four solvents; these changes were found to generally correlate with isothermal compressibility of the solvent. Slightly greater effects of pressure were observed for the polymeric stationary phase (4-7% change in order), with polar solvents inducing greater changes in order than nonpolar solvents. For both stationary phases, solvation was found to have a greater effect on conformational order than pressure. Collectively, these results were interpreted in terms of differences in the local surface bonding density and interchain spacing of the alkylsilanes of these two SPs.

The previous work on octadecylsilane SPs was extended to include detailed studies on a series of docosylsilane SPs also provided by Dr. Lane C. Sander of NIST. Raman spectral studies of the effects of temperature, surface coverage, polymerization method (surface or solution polymerized), nature of the alkylsilane precursor, and mobile phase solvent on conformational order in a series of high-density docosylsilane SPs ranging in surface coverage from 3.61 to 6.97 $\mu\text{mol}/\text{m}^2$ were completed.[18,23,24] Temperature-induced changes in order were observed between ~250 and 350 K for phases with surface coverage between 3.61 and 4.89 $\mu\text{mol}/\text{m}^2$. These changes occurred over a broad range of temperature characteristic of two-dimensional systems, but in general adhered to the behavior predicted for a simple first-order transition. This change is not believed to be an abrupt cooperative dissociation characteristic of a phase transition in a bulk phase, but instead is thought to involve significant changes in conformational order in segments of the surface-tethered molecules, mostly those segments at the outer edge of the alkylsilane. In contrast to the changes observed for surface coverage <5 $\mu\text{mol}/\text{m}^2$, a first-order change was not observed for the 6.97 $\mu\text{mol}/\text{m}^2$ phase. A molecular picture of the temperature-induced disorder

was proposed with disorder originating at the distal carbon and propagating only a short distance toward the proximal carbon.[18] Results on the docosylsilane systems were compared to those on the comparable octadecylsilane materials.

The effects of common solvents on alkyl chain conformational order in these docosylsilane SPs were also investigated by Raman spectroscopy.[23] Conformational order was evaluated using the intensity ratio $I[\nu_a(\text{CH}_2)]/I[\nu_s(\text{CH}_2)]$ as well as the frequencies at which these Raman bands were observed. Solvents studied include methanol- d_4 , acetonitrile- d_3 , water- d_2 , toluene- d_8 , chloroform- d and benzene- d_6 . Alkyl chain conformational order, and hence, solvation of the stationary phase, is found to depend directly on the Gibbs free energy change for dissolution of these molecules at infinite dilution into hexadecane from the gas phase ($\Delta G_{\text{HD}}^\circ$), as well as on stationary phase properties (polymerization method and surface coverage). In general, polar solvents with small positive values of $\Delta G_{\text{HD}}^\circ$ (i.e. unfavorable dissolution in hexadecane) increase slightly the conformational order of these docosylsilane SPs relative to their values in air, while nonpolar solvents with small negative values of $\Delta G_{\text{HD}}^\circ$ (i.e. favorable dissolution in hexadecane) decrease conformational order relative to the state in air by an amount proportional to $\Delta G_{\text{HD}}^\circ$. A comparison between docosylsilane and octadecylsilane bonded phase systems was made to further understand the role of alkyl chain length on solvent-stationary phase interactions. The change in alkyl chain conformational order induced by solvent was also compared to that induced by temperature, which provides insight into the effect of chromatographic conditions on stationary phase shape selectivity, an important application of these materials. Overall, these results suggest a partitioning mechanism for mobile phase solvent interaction with these docosylsilane stationary phases, even at very high surface bonding densities.

In previous work, the effects of aromatic compounds (toluene, benzene, p-xylene, anisole, aniline, and pyridine), temperature, and surface grafting method (surface or solution polymerized) on conformational order for the high-density octadecylsilane SPs were assessed.[15] Alkyl conformational order was found to decrease with decreasing surface coverage in these aromatic compounds, consistent with the behavior of these materials in air and in other nonpolar environments. However, despite the generally nonpolar characteristics of these media, the order of alkyl chains was found to exhibit a complex dependence on solvent hydrophobicity, hydrogen-bonding ability, and basicity. The most hydrophobic compounds impart disorder to the stationary phase, whereas hydrogen-bonding aromatics increase the order of homogeneous, high-surface coverage materials. Basic aromatic compounds increase the conformational order of both high- and low-coverage materials due to silanophilic interactions with exposed surface silanols. Molecular pictures of the chromatographic interface that display interactions between the alkyl chains and these aromatic compounds were proposed.

This work was extended by investigating the effects of four aromatic compounds on alkyl chain conformational order for the NIST series of high-density docosylsilane SPs.[24] Aromatic compounds studied include benzene- d_6 , toluene- d_8 , aniline- d_7 and anisole- d_8 . In general, these aromatic solvents decrease the conformational order of docosylsilane SPs relative to air suggesting interaction of these aromatic solvents with the SPs through partitioning into the alkyl chains, consistent with the conclusions from studies with the common solvents noted above. Changes in alkyl chain conformational order were found to be linearly dependent on the solvent hydrophobicity parameter $\log K_{ow}$, as well as on stationary phase properties (i.e. polymerization method and surface coverage). A comparison between docosylsilane and octadecylsilane bonded phase systems for these aromatic compounds was also made. The conformational order of the alkyl chains in a mixed solute/mobile phase system was also studied using 80% methanol/water as the mobile phase and aniline- d_7 , anisole- d_8 or toluene- d_8 as solutes. Collectively, the Raman spectroscopic evidence at the molecular level suggests that the interaction of these aromatic species with the bonded alkyl chains is through partitioning even at these high surface bonding densities.

Conformational order from Raman spectroscopy was correlated with chromatographic retention behavior for several high-density octadecylsilane stationary phase bonded layers.[31] These studies were performed in the presence of both mobile phase solvents and simple aromatic organic solutes (toluene, anisole, aniline) in order to gain insight into the mechanism of solute interaction at the stationary phase/mobile phase interface. Results were interpreted using classical chromatographic thermodynamic and kinetic descriptors of solute retention. It was found that solutes retained longer on these stationary phases generate greater conformational disorder of the stationary phase octadecyl chains. Chromatographic efficiency for aniline, a solute that undergoes exclusively silanophilic interactions, was poor with little structural consequence for the octadecylsilane stationary phase. This latter observation is consistent with penetration of these stationary phase layers only at sites devoid of octadecylsilane. This work is the first reported attempt to correlate directly vibrational spectral data with chromatographic retention.

This work correlating structural attributes extracted from Raman spectroscopy with chromatographic retention behavior for a series of solutes was extended to the high-density docosylsilane SPs as well.[31] Thermodynamic and kinetic parameters were extracted from the chromatographic behavior of aniline, anisole and toluene on a high-density docosylsilane SP with methanol/water as the mobile phase. Changes in SP structure in dilute solutions of these solutes in methanol/water were indicated by the Raman spectral order parameter; these changes were correlated with chromatographic retention. Raman spectral indicators obtained from the docosylsilane phase were correlated with capacity factors (k') and separation efficiency for each solute to provide insight into retention mechanism. Solute retention was found to depend on solute hydrophobicity as indicated by $\log K_{ow}$, as well as stationary phase polarity

gradient along the alkyl chain (i.e. perpendicular to the SP surface) in different mobile phase environments. As a result, the depth of penetration for each solute is different, leading to differences in alkyl chain conformational order, and therefore, different retention behavior.

Finally, initial Raman spectral studies on a series of mixed methylsilane/octadecylsilane stationary phases prepared by horizontal polymerization were completed.[33,34] Raman spectroscopy was used to examine the effects of temperature, surface coverage and solvent on the conformational order of octadecylsilanes in four horizontally-polymerized stationary phases prepared by modifying silica surfaces with different amounts of octadecyltrichlorosilane (C18 precursor) and methyltrichlorosilane (C1 precursor). As in our prior work, the conformational order of these stationary phases was assessed using the intensity ratios $I[v_a(\text{CH}_2)]/I[v_s(\text{CH}_2)]$ and $I[v(\text{C-C})_T]/I[v(\text{C-C})_G]$, and the frequency and full-width-at-half-maximum of the $v_a(\text{CH}_2)$ mode in their Raman spectra. Conformational order was found to increase with increasing C18 surface coverage and with decreasing temperature. C18 surface coverage was found to be a critical factor governing the conformational order of these stationary phases. Moreover, the conformational order of these stationary phases in solvents was found correlate with $\Delta G_{\text{HD}}^\circ$ as was observed for the conventional octadecylsilane and docosylsilane SPs discussed above. Low polarity solvents prefer to solvate these stationary phases in a partitioning process regardless of C18 coverage. For high C18 coverage phases, solvation by high polarity solvents generally occurs at the interface as an adsorption-like process. Finally, these horizontally-polymerized stationary phases were compared with conventional C18 stationary phases, and the conformational differences are used to account for different chromatographic performance of these two types of stationary phases.

As part of this work on horizontally-polymerized SPs, new Raman spectral peak fitting strategies had to be developed in order to eliminate spectral interference due to vibrational modes of the C1 species in the SPs that creates significant error in the spectral order parameters used to assess conformational order.[32] These new strategies were developed and validated utilizing a series of model alkyl chain systems that could be used predictively to accurately eliminate this spectral interference.

B. Raman Spectroscopy of Alkylsilane-Based Ion Exchange Stationary Phase Materials

Raman spectroscopy was performed on silica-based strong anion and cation exchange materials, Isolute, SAX and SCX-2, respectively, in aqueous solutions of different counter ions.[28] Raman spectral indicators were used to determine structural changes in surface-confined trimethylaminopropylsilane and propylsilylsulfonate groups of these ion exchange materials under conditions that mimic those used in ion chromatography. Observed structural changes were correlated with the selectivity of these materials for different counter ions. Results indicate that the strength of halide ion interaction with stationary phase

quaternary amine sites can significantly influence their structure in strong anion exchangers and that these interactions are a sensitive function of differences in ion hydration. However, oxyanions have little effect on quaternary amine structure despite large differences in selectivity, confirming the importance of hydrophobic exclusion effects as the basis of selectivity. In contrast to the behavior of the strong anion exchangers, little evidence of structure-altering interactions is observed for the sulfonate-based strong cation exchangers, substantiating the importance of hydrophobic contributions to selectivity for these systems.

This work was extended by investigating a silica-based strong anion exchange stationary phase in highly-concentrated aqueous electrolyte solutions of LiCl, LiNO₃, HCl and HNO₃ using Raman spectroscopy.[29] In these systems, the amount of water available for anion hydration was systematically changed by varying electrolyte concentration in ultrahigh ionic strength environments. For a given anion, the frequency of the $\nu_a(\text{CH}_3)_N$ mode of the stationary phase quaternary ammonium ion exchange sites was found to shift systematically with electrolyte concentration, with shifts in opposite directions for Cl⁻ and NO₃⁻. These frequency changes were correlated to anion hydration, thus providing spectroscopic evidence for the role of anion hydration in dictating interaction strength between an anion and the quaternary ammonium sites that define anion retention in these cation-exchange SPs. The information obtained in this study provides useful guidance for control of selectivity of stationary phase by manipulating the hydrophilicity of the stationary phase.

2. New Chromatographic Stationary Phases by Alcohol-Assisted Surface Templating (AAST)

A method for the preparation of silica-based alkylsilane stationary phases using octanol as a displaceable surface templates to control the rate of alkylsilane condensation with the silica surface, and thereby, the resulting alkylsilane surface coverage was developed.[17] This method improves upon conventional preparation schemes by allowing alkylsilane stationary phases of systematically varying surface coverage to be prepared from a single reaction mixture and a single precursor molecule without rigorous control of water content of the solution or of the silica. Octadecylsilane stationary phases ranging in surface coverage from ~3.5 to 6.0 $\mu\text{mol}/\text{m}^2$ were synthesized using one set of experimental conditions with variation of only the octadecylsilane:octanol ratio. The conformational order of the octadecylsilane alkyl chains was assessed using Raman spectroscopy and was found to increase with increasing surface coverage in a manner similar to stationary phases prepared by conventional routes. As chromatographic stationary phases in microbore columns for the reversed-phase separation of mono-substituted aromatic compounds, the performance of these materials was demonstrated to be comparable to or better than that of commercially-available octadecylsilane SPs under identical chromatographic conditions.

Furthermore, the high-density SPs ($>3.5 \mu\text{mol}/\text{m}^2$) prepared by this route were found to exhibit geometric shape selectivity comparable to or better than that reported earlier for high-density octadecylsilane SPs prepared using conventional methods.

Further efforts to define the mechanism whereby the displaceable alcohol template molecules act in controlling alkylsilane coverage were undertaken by investigating phases prepared using a series of n-alcohols from ethanol to hexadecanol as displaceable surface templates.[30] For an otherwise constant set of reaction conditions, octadecylsilane surface coverage of the resulting materials was found to decrease with decreasing alcohol chain length and increasing adsorption strength of the alcohol to the silica surface.

A mechanism by which control of surface coverage is achieved in AAST was proposed.[30] The monolayer of physisorbed n-alcohols controls the growth of a horizontally cross-linked alkylsilane monolayer at silica by restricting access to the underlying silanols. Desorption of alcohol molecules to expose reactive sites serves as a kinetic and thermodynamic barrier to alkylsilane condensation reactions with the surface silanols. Thus, the alkylsilane surface coverage is controlled by K_{ads} . In order to obtain stationary phases with high surface coverage and concomitant high conformational order, displaceable surface templates with smaller K_{ads} should be used. Conversely, disordered stationary phases of relatively lower surface bonding density can be achieved using alcohol templating molecules with larger K_{ads} values.

SPs fabricated by this approach were demonstrated using chromatography to be as good as or better than SPs prepared by conventional routes.[30] Specifically, SPs prepared by the new method exhibit comparable to or better shape selectivity than similar phases prepared by conventional methods, especially those phases with lower surface coverage.

3. Interfacial Molecular Structure of Mobile Phases at Chromatographically-Relevant Modified Silica Surfaces

A. Development of Novel Ultrathin Silica Films Supported on Metals as Substrates for Reflectance-Based Spectroscopies

Work continued in this funding cycle on developing ultrathin silica films supported on metals for a variety of uses related to understanding interfacial structure-function relationships in chromatography. Past work supported on earlier DOE grant awards led to the development of a scheme for coupling ultrathin ($<10 \text{ nm}$) sol-gel silica films with Ag and Au substrates through a hydrolyzed and cross-linked self-assembled monolayer of (3-mercaptopropyl)trimethoxysilane (3MPT). However, in addition to producing spectral

interference for use of these films in surface vibrational spectroscopy studies, it was also thought that this 3MPT layer might be chemically labile under certain conditions. The strength and robustness of bonding of the 3MPT layer to underlying Ag substrates was investigated using electrochemical underpotential deposition of monolayers of Pb and Tl.[21] Based on the observation of negative potential shifts for their underpotential deposition processes, Tl and Pb undergo underpotential deposition directly on the underlying Ag surface by insertion between the Ag-S bond. This process was proposed to occur by penetration of the 3MPT monolayer by the hydrated metal ions through spaces in the six-membered siloxane rings that form at the terminus of the 3MPT layer after hydrolysis and condensation. In contrast, Cd does not undergo similarly facile underpotential deposition at 3MPT-modified Ag electrodes due to a hydrated ion size too large to fit through these openings. The voltammetric evidence suggests hydrated metal cation size as described by the Stokes diameter is the primary determinant of Ag electrode accessibility for UPD through the cross-linked 3MPT layer. This assertion was further supported by molecular mechanics energy minimization computations of six-membered siloxane rings on each of the three low index faces of Ag.

Significantly, these metal monolayers deposit *under* the 3MPT layer on Ag by cleaving the Ag-S bond and creating a new metal-S bond; this observation suggests that the Ag-S bond is relatively labile. Despite this lability, the 3MPT layers were found to be exceptionally stable to repeated electrochemical deposition and stripping of these metal layers through hundreds of cycles, presumably due to the enhanced stability afforded by cross-linking the 3MPT molecules through siloxane bonds at the distal edge of the layer.[21] This stability in the presence of underpotential deposition is in marked contrast to the behavior of simple alkanethiol self-assembled monolayers of comparable length, which are displaced by metal underpotential deposition of Pb and Tl within a few deposition-stripping cycles.

Covalent attachment of ultrathin silica films (thickness <10 nm) to gold substrates through a new wetting control and adhesive layer, a hydrous gold oxide layer, was also achieved as part of this grant award.[22] Silica layers were prepared using spin-coating of sol-gel precursor solutions onto gold substrates that were cleaned and oxidized using UV photo-oxidation in an ozone atmosphere. The gold oxide layer resulting from this process acts as a wetting control and adhesive agent for the ultrathin silica layer. This approach overcomes stability problems and spectra interference caused by use of a similar wetting control and adhesive layer of (3-mercaptopropyl)trimethoxysilane. Control of the thickness of ultrathin silica layers deposited on top of the gold oxide by a sol-gel method is achieved between 6-60 nm through modification of precursor solution composition or by repetitive deposition. The resultant ultrathin silica films were characterized using infrared spectroscopy, ellipsometry, atomic force microscopy, and cyclic voltammetry. For the standard deposition parameters developed as part of this work, the films were determined to be stable in aqueous solutions ranging from pH from 2 to 9 for hours and in solutions of

pH 10 for up to 30 min. Finally, these ultrathin silica films were modified with self-assembled monolayers of octadecylsilane, demonstrating the surface chemistry of bulk silica.

These ultrathin silica films were demonstrated to contain nanoscopic defects.[22] In all cases, these defects were of radii $\leq 2 \mu\text{m}$, and were present in these films at a density of 1.6 defects per $10 \mu\text{m} \times 10 \mu\text{m}$ region, with a weighted average defect radius of $\sim 200 \text{ nm}$. This array of defects was shown to exhibit a voltammetric response consistent with ultramicroelectrode arrays. These pinholes were shown to be passivated via electrochemical polymerization of phenol to create insulating poly(phenylene) oxide plugs as documented by atomic force microscopy and infrared reflectance-absorbance spectroscopy. Passivation of pinholes is $\sim 99.5\%$ complete after 550 voltammetric cycles of oxidative electropolymerization.[25]

Due to the excellent control of thickness of these ultrathin silica films, they could be used effectively as probes of the distance dependence of surface enhanced infrared absorbance (SEIRA).[36] Systematic and controlled variation in silica layer thickness, along with the probe molecule p-nitrobenzoic acid (PNBA), allows definition of the distance dependence of SEIRA on these substrates and the maximum enhancement operative. The observed distance dependence for these substrates is in good agreement with previous reports. Thus, the substrate system described herein offers a straightforward and well-defined silica substrate that can be readily coupled with SEIRA experiments in the reflectance mode.

B. Interfacial Structure of Mobile Phases on Silica and Alkylsilane-Modified Silica Surfaces using Infrared Reflectance-Absorbance Spectroscopy in the Forced Dewetting Geometry

An important achievement of the previous funding period was the use of these ultrathin silica films in IRRAS studies in which residual fluid films created by forced dewetting were studied. This approach has been demonstrated in this laboratory to create residual films typically $< 10 \text{ nm}$ in thickness which are contain inherently interfacial fluid molecules that can be probed with vibrational spectroscopy to lend insight into interfacial structure-function behavior. Two studies were completed using this approach that are relevant to chromatographic systems.

The structure and thickness of residual interfacial water layers formed by forced dewetting of model silica-water interfaces as a function of solution pH were investigated using IRRAS and ellipsometry.[37] The structure of the interfacial water layers in all cases was found to be considerably more ordered than isotropic water layers from solutions of comparable pH whose spectra were simulated from spectral parameters of the bulk solutions. The thicknesses of these residual layers were found to be pH dependent and vary from ~ 6 (at pH 1), up to $\sim 9 \text{ nm}$ (at pH 5.6). These thickness were determined to

reflect a combination of van der Waals (according to Lifshitz theory), structural (hydration), and electrostatic force contributions to the disjoining pressure, which controls films thickness under conditions (e.g. very small capillary numbers) in which hydrodynamic contributions to interface formation are negligible. Although van der Waals and structural forces contribute for solutions of all pH, electrostatic force contributions to the disjoining pressure are only significant at charged silica surfaces at pH values $>pK_a$ for the surface silanols. Thus, due to this additional contribution to the total disjoining pressure at $pH > 6$, the residual films observed are $\sim 50\%$ thicker.

The second study involved investigation of residual layers of methanol-water “mobile phases” at silica surface modified by octadecylsilane self-assembled monolayer “stationary phases.”[38] Unfortunately, exhaustive investigation of such complicated systems was found to be limited by the sensitivity of the composition of the residual layers to the ambient solvent vapor phase composition. Specifically, the spectral responses proved that changes in vapor phase composition resulted in either deposition and/or evaporation of the solvent vapors into or from, respectively, the residual layers with the direction of transfer dictated by the excess of a given component in either phase. Nonetheless, useful insight into unique interfacial intermolecular interactions was provided by these studies. Methanol molecules were found to experience significant changes in their hydrogen bonding in these residual layers as a function of gas phase composition. As expected, for water-rich residual layers, hetero-hydrogen bonding between methanol and water dominates the spectral response. In contrast, for methanol-rich residual layers, homo-hydrogen bonding between methanol molecules was mostly observed. In general, this observation indicates that the composition and chemical environment of residual solvent layers from a binary mixture can be modified by changing the composition through control of the vapor phase composition. No unique vibrational behavior attributed to specific chemical interactions between either mobile phase solvent and the octadecylsilane stationary phase were observed. This observation is consistent with the results of the studies on conventional stationary phases described above in which neither methanol nor water had any significant effect on the conformational order of the stationary phase alkyl chains.

4. Modeling Porosity in Chromatographic Stationary Phase Supports using Colloidal Arrays of Controlled Sub-100 nm Silica Nanoparticles

Despite the fact that the pore size and porosity of stationary phase support materials in modern packed-bed chromatographic separations have always been recognized as critical attributes, a clear understanding of the fundamental chemical structure and dynamics within the constrained environment of the intraparticle pore space has not been achieved yet would seem to be essential for significant advances in chromatographic methods. Toward this end, we initiated studies to use thin colloidal

crystalline arrays (CCAs) composed of silica nanospheres to produce assemblies of pores with highly uniform size and volume that can be probed with vibrational spectroscopies.

In order to create such arrays with pore sizes relevant to these chromatographic stationary phases, very small silica particles are needed. At the outset of this work, robust strategies for reproducible production of spherical (essential for crystalline packing) sub-100 nm silica nanoparticles did not exist. Thus, in our initial efforts, we developed a strategy for production of monodisperse spherical sub-100 nm silica particles based on application of a conceptual modification of the classic LaMer model to the Stöber process.[26] Strategies for control of particle properties, including particle size, size distribution, and shape were proposed and rationalized based on this modified LaMer model. This approach started from a small number of test experiments to make particles with defined properties from which reaction condition adjustment could be undertaken to control undesirable particle properties of the resulting particles while leaving conditions that dictate desirable properties unchanged. This strategy reduced considerably the number of test experiments required for synthesis of uniform and spherical sub-100 nm silica particles compared to other methods reported that utilize a large number of test experiments to define optimized reaction conditions. Synthesis of particles in the size range of 27 to 100 nm with relative standard deviations in size of <13.3% was demonstrated by application of this strategy.

In follow-on work, self-assembly of sub-100 nm spherical silica nanoparticles into ordered, tightly-packed three- and two-dimensional arrays was achieved.[27] Self-assembly by vertical evaporation was investigated for particles made by two methods: an optimized Stöber method recently reported from this laboratory and a modified reverse micelle method. Ordered, close-packed, two- and three-dimensional structures were formed with spherical nanoparticles made by the optimized Stöber method. Fast Fourier transforms of top-view scanning electron microscopy images documented close-packed hexagonal packing for three-dimensional arrays consisting of particles as small as 50 nm. Ranges over which evaporation temperature and suspension particle concentration can be altered as strategies for improving packing quality of 50 nm particles were defined. Self-assembly behavior that is distinct from that of larger particles (>200 nm) was observed for these sub-100 nm particles in that the ranges over which these variables can be altered to affect array packing quality are much smaller than for larger particles. In contrast, for particles made by the reverse micelle method, only structures with poor packing quality were obtained despite the fact that such particles are typically more uniform than those made by the Stöber method. These results provided clear evidence that, in addition to particle uniformity, other particle properties deriving from fabrication method play important roles in directing self-assembly of sub-100 nm particles. Finally, a rapid self-assembly method based on horizontal evaporation was used to produce close-packed three-dimensional structures of these sub-100 nm particles spanning several millimeters. Although these arrays are not as ordered as those made by vertical evaporation, the strategy

developed allows tightly-packed, crack-free arrays up to microns in thickness to be fabricated. A mechanism for self-assembly by this process was proposed.

These arrays were utilized for the measurement of diffusion coefficients of molecules in the nanopores. [35] This approach taken was to deposit an ordered packed colloidal array thin film with well-defined pore structure onto FTIR-ATR internal reflection element and to utilize FTIR-ATR for collection of in-situ kinetic information. A model was developed for calculation of diffusion coefficients from these data with the aid of computer simulation. Results on diffusion of hexane and hexadecane in acetonitrile in the nanopores of the colloidal array indicate a decrease of up to 8 orders of magnitude in diffusion coefficient in the nanopore system compared to diffusion in bulk solution. Based on our experiments and the results published by other groups, we concluded that, at this pore size scale, rather than molecule-to-pore size ratio, interaction with the pore walls due to physical confinement is the major factor that dominates the diffusion of molecules in such nanopores.

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29. Y. Huang, J.E. Pemberton, *Chromatographia*, submitted. Characterization of Strong Anion Exchange Stationary Phases in Highly Concentrated Chloride and Nitrate-Containing Aqueous Electrolytes by Raman Spectroscopy.
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33. W. Huang, L.C. Sander, J.E. Pemberton, in preparation. Effect of Temperature on Alkyl Chain Order of Mixed Methylsilane-Octadecylsilane Stationary Phases formed by Horizontal Polymerization.
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35. Y. Huang, J.E. Pemberton, in preparation. Mass Transport of Organics through Tightly-Packed Colloidal Arrays of 50 nm Spherical Silica Nanoparticles.
36. P. Macech, J.E. Pemberton, in preparation. Distance Dependence of Surface Enhanced Infrared Absorption Spectroscopy on Ultrathin Silica Films Supported on Reflective Gold Substrates.
37. A. Mudalige, P. Macech, J.E. Pemberton, in preparation. Residual Water Layers on Silica Surfaces Formed by Forced Dewetting from Aqueous Solutions of Different pH.
38. A. Mudalige, P. Macech, J.E. Pemberton, in preparation. PM-IRRAS of Thin Residual Films of Methanol-Water Mixtures on Octadecylsilane-modified Silica Surfaces Formed by Forced Dewetting.

Presentations from DE-FG03-95ER14546 (P Poster, * Invited)

^PM. Cai, J.E. Pemberton, 210th National Meeting of the American Chemical Society, Chicago, IL, August 1995. Surface Raman Spectroscopy of Molecules on Thin Sol-Gel Silica Films Immobilized on Ag Surfaces.

^PM. Ho, J.E. Pemberton, 213th National Meeting of the American Chemical Society, Las Vegas, NV, September 1997. Raman Spectroscopic Characterization of Commercial Reversed-Phase Liquid Chromatography Stationary Phases.

^PM. Cai, M. Ho, J.E. Pemberton, 213th National Meeting of the American Chemical Society, Las Vegas, NV, September 1997. Raman and FTIR Spectroscopy of Layered Structures Formed from Alkylsilanes Bonded to Self-Assembled Monolayers of (3-Mercaptopropyl)trimethoxysilane on Ag.

*J.E. Pemberton, Symposium on Surface Analysis in Separation Science, California Separation Science Society Meeting, San Jose, CA, February 1998. Characterization of Liquid Chromatography Stationary Phases using Raman Spectroscopy.

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^PC.J. Orendorff, M.W. Ducey, J.E. Pemberton, 221st National Meeting of the American Chemical Society, San Diego, CA, April, 2001. Structure-Function Relationships of Octadecylsilane Stationary Phases by Raman Spectroscopy.

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Z. Liao, A. Ange, C.J. Orendorff, J.E. Pemberton, 229th National Meeting of the American Chemical Society, Washington, DC, August 2005. New Alkylsilane Stationary Phases of Controlled Surface Coverage through Displaceable Surface Templates Based on n-Alcohols.

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