TIME-RESOLVED ANALYTICAL METHODS FOR
LIQUID/SOLID INTERFACES

Progress Report

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Progress Report Abstract

A number of chemical phenomena that occur at the boundaries between insulating solids and liquids (adsorption, partition, monolayer self-assembly, catalysis, and chemical reactions) are important to energy-related analytical chemistry. These phenomena are central to the development and understanding of chromatographic methods, solid-phase extraction techniques, immobilized analytical reagents, and optical sensors. The goal of this program, therefore, is to develop surface-sensitive spectroscopies by which chemical kinetics at liquid/solid interfaces can be observed on time-scales from nanoseconds to seconds. In the second year of this program, we have used temperature-jump relaxation measurements of adsorption/desorption kinetics at liquid/solid interfaces out using Joule heating to kinetic barriers to compare the adsorption of ions from solution onto C1- and C4-derivatized silica surfaces. We completed a study of rate of migration of covalently-attached ligands on silica surfaces; from the temperature-dependence of the migration, the large energy barrier to migration was estimated. Surface heterogeneity of adsorption sites on silica was characterized by time-resolve fluorescence, and the chemical origins investigated by Si^{29} nmr spectroscopy. Surface-enhance Raman and fluorescence spectroscopies were modified to study adsorption and binding to silica surfaces. Molecular dynamics simulations were started to help better understand kinetic barriers to adsorption; esr probe measurements were launched to measure and compare the chain mobility of silica-attached alkyl ligands.

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Most of our understanding of chromatographic processes has been inferred from retention measurements. These measurements do not generally provide information about the role of sorption and desorption kinetics on retention equilibria. In the second year of this project, we have used temperature-jump relaxation techniques to monitor reversible kinetics at the liquid/solid interface. A Joule-discharge apparatus was used to heat a packed bed of porous silica gel on a microsecond time scale. We completed our study of sorption/ desorption relaxation kinetics for a fluorescent probe, 1-anilino-8-naphthalene sulfonate (ANS) at a C18-modified silica surface. On a 100 μ s time scale, a biexponential relaxation was detected, where the slow rate increased as retention of the solute was increased (by changes in mobile phase composition). This behavior suggested that sorption kinetics were controlling the relaxation rate; the linear dependence of the rate on the concentration of the probe in the mobile phase verified this postulate. The results showed further that the sorption rate of this ionic probe is slower than diffusion-limited and exhibits significant influence over the equilibrium constant. The sorption rates of two neutral probes, however, were indistinguishable from a diffusion limit indicating a negligible barrier to sorption.

A second study of adsorption kinetics of ANS onto a C1-derivatized silica surface showed that a similar slow adsorption rate arose from the adsorption of ionic solutes from solution. These results helped us understand the origins of the two steps for sorption onto longer chain ligands on silica surfaces. For adsorption of neutral probes onto a C1-surface, no barrier could be detected. To compare the response of an intermediate chain-length surface, we measured adsorption/desorption relaxation kinetics for the charged fluorescent probe, 1-anilino-8-naphthalene sulfonate (ANS) at C4-derivatized silica. A bi-exponential relaxations was detected having comparable rates that linearly increase as solute concentration; this behavior suggested that adsorption kinetics on the intermediate chain length interface are different from the kinetics on both C1 and C18 surface. The relaxation rate of a neutral probe, N-phenyl-1-naphthylamine (1-NPN) was also measurable in our experiments, which indicate the kinetic barrier to sorption cannot be neglected as in C1 and C18 cases. This results show that alkyl-chain length on silica-modified surfaces can produce different underlying kinetic mechanisms.

To better understand the effect of chain-length on ligand mobility, molecular dynamics simulations were started to study the conformation, interactive process dynamics of n-alkyl bonded phases which relate to the retention mechanism. Three systems have been constructed which corresponded to ligand chain lengths of C4, C8 and C18 with $3.0 \mu\text{mol}/\text{m}^2$ surface coverage. A number of parameters related to the structure of the stationary phase will be derived in order to characterize the molecular properties of each system. These parameters include the hydrocarbon layer thickness, the fraction of gauche conformations, the distance distribution for carbon atoms and the diffusion coefficients of individual atoms. From these properties, the orientations of chains with respect to the surface as well as their mobility can be estimated.

To experimentally probe the chain motion on the sub-nanosecond time scale of molecular dynamics simulations, electron spin resonance spectroscopy with a spin probe technique can be used to determine surface solvation and solute-surface interactions. Line width analysis in the fast motional regime can yield a mean rotational correlation time, τ , and rotational anisotropy factor, N , that can demonstrate motional constraints that the host medium places on the probes and thereby indicated how the probe is constrained geometrically by the host. Thus far in our work, the spin probe 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) has been used. The alkyl bonded phases, C1, C4, C18 were synthesized and were identical to those samples used in the temperature-jump kinetics and chromatographic retention measurements. For the TEMPO probes interacting with bonded silica of various chain lengths, the coupling constants, line width and amplitude values can be obtained from the experiments. Our initial results show that the line widths and line shapes undergo significant changes from free methanol/water solution to modified silica surface, and the width of the central line is broader in the presence of the modified surface. The changes result from decreased rotational mobility and an increase in the rotational anisotropy of the probe.

Also during the second year of this project, we completed our study of surface migration of chemisorbed or covalently bound ligands on silica surfaces was quantified, and the rate of migration was determined. A slow growth of excimer fluorescence emission was observed after exposing silica samples (sparingly-derivatized with 3-(1-pyrenyl)-propyl-dimethylmonochlorosilane (3PPS)) to either water vapor or aqueous solution. Initially, there

was no detectable excimer emission from the sample because the submonolayer coverages result in 3PPS ligands that are widely dispersed on the surface. The slow appearance of excimer emission after exposing the sample to water indicated that 3PPS molecules migrate along the surface; 3PPS ligands were not significantly hydrolyzed from the surface as revealed by solubility tests. The time evolution of the excimer emission was measured and successfully modeled using a two-dimensional diffusion theory; the values of surface diffusion coefficients for chemisorbed species were obtained along with estimates of the encounter radius. The migration could be arrested by blocking adjacent silanol bonding sites with trimethylsilyl groups. The temperature-dependence of the migration rate was also investigated, and the activation barrier to surface diffusion was determined.

Related to the study of migration between binding sites on silica, inhomogeneous fluorescence decay kinetics were observed from the 3PPS probe covalently bound to silica surface. The fluorescence decay kinetics were found to follow a discrete population model rather than a continuous lifetime distribution model and were attributed to the energetic heterogeneity of the silica surface. The existence of two silanol sites on silica surface was further supported by the fact that pyrene probe molecules were bound to different surface environments, revealed by their difference in fluorescence decays when a chlorosilane verses a hydroxysilane reagent is used. It was also found that, when using chlorosilane, the fluorescence decay became more heterogeneous when increasing the reaction time or exposing the derivatized sample to water. These results can be explained by a selective reaction between the hydroxysilane and a small population of active silanols, while chlorosilane reacts rapidly with all type of silanols under kinetic control. Fluorescence quenching studies of surface-immobilized pyrene by iodine and mercury chloride were also conducted; enhanced quenching rates for the shorter-lived excited-state population were observed and attributed to the adsorption of quencher molecules to the same active silanol sites which also caused a faster decay rate for some of the surface-bound pyrene probes.

To understand the chemical origins of the site heterogeneity, solid-state ^{29}Si NMR was used to distinguish between geminal and monomeric silanols and study the relative reactivity of these silanols to chloro- and hydroxysilane reagents. Chlorosilane were found to react preferentially with geminal

SERS response, we have begun a study of adsorption kinetics of surfactants onto oxide surfaces. Surfactants are used in energy-related mineral processing as drilling lubricants, corrosion inhibitors, and for particle isolation. Developing an understanding of the interactions of surfactant molecules with oxide surfaces would have practical importance. In this study, the formation of surfactant monolayers on a model silica surface was monitored with SERS. Raman scatter is generated by cylindrically focused, front-surface illumination of the SERS substrate, is collected, collimated, and focused onto the entrance slit of a single-stage monochromator, and is detected with a charge-coupled device detector. The adsorption kinetics of cetylpyridinium chloride (CPC), a cationic surfactant prominently used in froth or ion flotation separation of minerals, have been attained at CPC concentrations below the critical micelle concentration (0.9 mM). CPC is a molecule comprised of a hydrophilic pyridine head group and a hydrophobic 16-carbon tail. The Raman intensity of the 1027-cm^{-1} ring-breathing mode of CPC was measured as a function of time. Our results, which differ from previous predictions based on isotherm data and speculation, resemble a 2-stage Langmuir adsorption kinetics, suggesting that CPC forms a complete, closely-packed monolayer before subsequent adsorption of a second monolayer, forming a tail-to-tail bilayer.

Additional tools for investigating adsorption and binding chemistry include surface enhanced fluorescence and absorption spectroscopy; these phenomena are complex owing to the interaction between electronic excited states and the underlying metal island surface. A better understanding of their properties will allow for their use as surface analytical tools with increased sensitivity compared to SERS for surface-bound species. Studies are done on an SiO_2 surface because of the application of the surface chemistry to chromatographic systems and the ease of forming a reference surface identical to the surface under study but without any enhancement. A 35 Å silver island film forms a substrate for surface enhanced spectroscopy; onto this, 45 Å layer of SiO_2 is deposited. The organosilane, 4-aminobutyldimethylmethoxy-silane is used to modify the surface for the selective adsorption of different quantum yield isothiocyanate dyes: fluorescein ITC, eosin ITC, and erythrosin ITC. The initial absorbance spectra of both the silver film and the dye alter the shape of the enhanced absorbance of the surface during formation of a dye

surface layer. The effects of silver island films with different absorption maxima as well as different dye absorption maxima were studied; in part, this data supports the theoretical enhanced absorbance calculated by Weitz et al. The concentration of the dye solution and the SiO_2 layer thickness also influence the absorbance spectrum of the surface. Similarly, the enhanced fluorescence of the dye as it adsorbs to the surface is shown to be dependant on the concentration of the dye solution as well as on the quantum yield of the dye. A photobleaching study, varying the dye as well as surface dye concentration was done to better understand the effects of the silver underlayer.

To test the binding of organosiloxane compounds to a silica surfaces (creating selective adsorption of target compounds to a silica surface), a referee method with known response sensitivity and surface selectivity was needed. External reflection FT-IR spectroscopy (ERS-IR) can detect single monolayers on reflective surfaces. This technique allows for the study of interfacial binding kinetics and is a method for quantifying of surface concentrations because the absorbance is independent of surface concentration. The experimental design that yields sub-monolayer detection with consistent spectral intensities is under study. A 45 Å layer of SiO_2 is deposited on an optically-thick coating of silver to allow for the study of interfacial silane chemistry. The organosilane, 4-aminobutyldimethyl-methoxysilane is bound to the SiO_2 surface to give an amine functionality at the interface. The rate of binding of this silane was studied through an ex-situ ERS-IR experiment. The adsorption and binding of isothiocyanate-derivatized dye molecules to the aminated surface is also under study using this technique.

The new area we plan to open up in the next year relates to investigating rates and mechanisms of irreversible reactions at liquid/solid interfaces such as binding reactions, irreversible adsorption, and conformational changes. The approach we are planning for these applications adapts stopped-flow kinetic methods to surface chemistry. Flow methods for porous substrates are generally slow due to the long time required for diffusion into the particle interior. We propose instead to carry out stopped-flow measurements on suspensions of pyrogenic or fumed silicas; rapid mixing of particulate slurries or model silica compounds with reactive solutions will be possible by using a stopped-flow apparatus which we adapted to fluorescence detection.

Personnel Supported on DOE Grant

Students who have been working on this project during the past year include: Haibo Wang, graduate student who earned his Ph.D in August; William Lacy, Ph.D. student; Lydia Olson, Ph.D. student; and Feiyan Ren, Ph.D. student.

Scientific Publications from DOE-Sponsored Research (cumulative 3/92 - 10/94)

1. "Electronic Spectroscopic Investigations of the Stationary Phase in Reversed Phase Liquid Chromatography", S. C. Rutan and J. M. Harris, J. Chromatogr. **656**, 197 (1993).
2. "Joule-Discharge Heating Studies of Pore Connectivity in Silica Gel: Influence of Pore Diameter, Chemical Modification, and Particle Size", E. H. Ellison, S. W. Waite, D. B. Marshall, and J. M. Harris, Anal. Chem. **65**, 3622 (1993).
3. "Temperature-Jump Investigation of Sorption/Desorption Kinetics at Reversed-Phase Chromatographic Silica/Solution Interfaces", S. W. Waite, D. B. Marshall, and J. M. Harris, Anal. Chem. **66**, 2052 (1994).
4. "Lateral Diffusion of Covalently-bound Siloxane Molecules on Silica Surfaces", H. Wang and J. M. Harris, J. Amer. Chem. Soc. **116**, 5754 (1994).
5. "Laser Temperature-Jump Relaxation Measurements of Adsorption/Desorption Kinetics at Liquid/Solid Interfaces", S. W. Waite, J. F. Holzwarth, and J. M. Harris, Anal. Chem. (submitted, in review).
6. "Temperature-Jump Investigation of Adsorption/Desorption Kinetics at C1 Reversed-Phase Chromatographic Silica/Solution Interfaces", F. Y. Ren, S. W. Waite, and J. M. Harris, Anal. Chem. (to be submitted 11/94).
7. "Origins of Bound-probe Fluorescence Decay Heterogeneity in the Distribution of Binding Sites on Silica Surfaces", H. Wang and J. M. Harris, (in preparation, 2nd draft, copy available).
8. "Solid-State ^{29}Si NMR Study of Binding and Migration of Siloxane Ligands at Silica Surfaces", H. Wang and J. M. Harris, (in preparation, 2nd draft, copy available).

P.I. Invited Lectures Reporting DOE-Sponsored Research

1. "Molecular Transport and Kinetics at Liquid/Solid Interfaces", Occidental Chemistry Colloquium Lecture, SUNY Buffalo, November 5, 1993.
2. "Temperature-jump Investigation of Adsorption/Desorption Kinetics at Methylated Silica/Solution Interfaces", Engineering Foundation Conference on Surface Characterization of Adsorption and Interfacial Reactions, Kona, January 10, 1994.
3. "Surface Binding, Heterogeneity, and Migration of Siloxane Ligands on Silica", 3rd Symposium on Molecular Reaction Dynamics in Condensed Matter, Salt Lake City, April 7, 1994.
4. "Fluorescence Studies of Surface Binding, Heterogeneity, and Migration of Siloxane Ligands on Silica", 36th Rocky Mountain Conference on Analytical Chemistry, Denver, August 1, 1994.
5. "Transport and Kinetics at Liquid/Solid Interfaces", Invited Lecture Series, University of Colorado, Boulder, August 4, 1994.
6. "Reaction Kinetics at Liquid/Solid Interfaces", Invited Lecture Series, University of Colorado, Boulder, August 5, 1994.

Papers Contributed to Scientific Meetings Reporting DOE-Sponsored Research

1. "Temperature-jump Investigation of Adsorption/Desorption Kinetics at Methylated Silica/Solution Interfaces", F. Y. Ren, S. W. Waite, and J. M. Harris, 3rd Symposium on Molecular Reaction Dynamics in Condensed Matter, Salt Lake City, April 7, 1994.
2. "Monitoring Adsorption Kinetics at Oxide Surfaces using SiO₂ Overcoated Silver as a SERS Substrate", W. B. Lacy and J. M. Harris, 208th National ACS Meeting, Washington, DC, August 21, 1994.