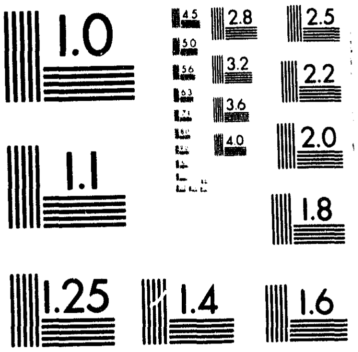
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TIME-RESOLVED ANALYTICAL METHODS FOR LIQUID/SOLID INTERFACES

Progress Report

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TIME-RESOLVED ANALYTICAL METHODS FOR LIQUID/SOLID INTERFACES

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. Chemical interactions which govern in these processes cannot generally be identified solely by equilibrium measurements of surface concentrations, since the steady-state behavior of the system does not reveal the mechanism or rates of surface reactions. 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 first year of this program, we have used Joule-discharge heating kinetics to study the pore structure of silica gels; the effects of pore diameter, particle size, and chemical modification on the pore connectivity were investigated. Temperature-jump relaxation measurements of sorption/desorption kinetics at liquid/solid interfaces were also carried out using Joule heating; kinetic barriers to sorption of ions from solution were found for both C18 and C1 surfaces. Through a collaboration with the Fritz-Haber Institute in Berlin, we were able to acquire the first laser temperature-jump data on kinetics at liquid/solid interfaces by using a colloidal sample. We also quantified the 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. Finally, a review of the applications of electronic spectroscopy (absorption and fluorescence) to the study of reversed-phase chromatographic interfaces was published.

NOTICE

Studies of Joule-discharge heating of packed beds of chemically-modified silica gel were carried out to determine the influence of pore diameter, particle size, and chemical modification on the heating kinetics of the silica gel. The results revealed that surface modification and pore diameter affect the connectivity of the intraparticle pore network. Heating of packed beds consisting of 60 µm, 100 µm, and 147 µm pore-diameter silica gels modified with n-triacontyldimethylsilyl (C30), dimethyloctadecylsilyl (C18) or trimethylsilyl (C1) ligands were monitored by observing the temperature-dependent fluorescence of NBD-hexanoic acid in MeOH/H_2O solvents. A decrease in the silica pore diameter, an increase in the length of surface ligands, or an increase in bonding density of the ligands caused a reduction in the rate of the energy dissipation in the temperature-jump cell. The temperature equilibration time or minimum heating time, τ_h,min, depended on particle size with 5 µm, 10 µm, and 40-63 µm octadecylsilica exhibiting $_h$,min values of ca. 5 µs, 10 µs, and 250 µs, respectively. Joule-heating at a discharge rate of 2×10^5 s^{-1} of 5 µm and 10 µm silicas was uniform as indicated by a single exponential response of the fluorescence thermometer; while a bi-exponential response for larger particle silica showed evidence of non-uniform heating. The rate and uniformity of heating depend upon the particle size and length of the alkyl ligands attached to the surface.

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 first year of this project, we have shown that temperature-jump relaxation techniques can be used 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 observed sorption/desorption relaxation kinetics for a fluorescent probe, 1-anilino-8-naphthalene sulfonate (ANS) at a C18-modified silica surface. On a 100 µs time scale, a slow relaxation was detected having a rate that 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. While sorption kinetics do not often play a significant role in band broadening, these results show that their influence on the equilibrium constant cannot be overlooked and that similar retention equilibria can arise from vastly different underlying kinetic mechanisms.

Laser temperature-jump experiments to measure adsorption/desorption kinetics at liquid/solid interfaces were performed at the Fritz Haber Institute of the Max Plank Society in Berlin. Bi-exponential relaxation traces were observed in absence of electrolyte on C1 fumed silica, while the addition of NaCl caused the relaxations to become much more single exponential. These results along with the isotherm and chromatographic peak shapes show that there are two or more sorption sites for ANS on a C1 silica. In the absence of electrolyte, the two sorption site mechanism is caused by a non-uniform distribution of residual surface silanols. The addition of NaCl decreases the thickness of the electrical double layer caused by the silanol sites, provides counter ions to neutralize the silanol charge, and creates an energetically more homogeneous surface. Sorption rate constants were calculated, and it was shown that kinetics of sorption and desorption can effect the chromatographic peak shape.

Also during the first year of this project, the first observation 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.

As an additional product of the first-year activities, an invited review was written in collaboration with Prof. Sarah Rutan from Virginia Commonwealth. The manuscript covered the electronic spectroscopy of probe molecules used to characterize structure and dynamics of reversed-phase liquid chromatographic interfaces.

Plans for several research projects to begin in the second year of this grant are as follows. We propose to investigate how the migration of bound ligands on silica surfaces changes the environment of those ligands and the adsorption characteristics of the surface. Since the initial surface that we prepare is metastable, we plan to use ^{29}Si nmr to look for differential silanol reactivity affecting the final distribution of surface-bound ligands following migration.

The nature of longer-range diffusion of molecules through liquid-filled porous solids is not well-characterized, especially in the distance range of 1 - 10 μm; this is a very important distance range in terms of transport contributions to the efficiency of chromatographic and catalytic materials. Measuring the quenching kinetics of luminescent probes offers a simple approach to determining longer-range diffusion rates in porous solids and, more importantly, exploring the effects of pore diffusion on encounter rates of molecules with surface sites. Since the distance scale of quenching measurements is governed by the diffusion of molecules over the lifetime of the excited state probe, to observe long-range transport requires that a long-lived excited state be generated. We plan to examine quenching of long-lived excited-triplet states of acridine or aromatic ketones such as benzophenone within porous silica matrices; these molecules exhibit a triplet lifetimes greater than 100 μs in fluid solution at room temperature. We have experience detecting weak, long-lived phosphorescence of aromatic ketones in fluid solution which provides a convenient method of measuring the decay of the excited state population; for acridine, we could observe fluorescence from triplet-triplet annihilation when acridine is the diffuser. Efficient quenchers could be oxygen, simple conjugated dienes and trienes, biacetyl, or aromatic hydrocarbons which have lower energy triplet states and thus promote rapid triplet energy transfer.

A new method of studying desorption kinetics at dielectric solid surfaces is also proposed for investigation, based on a dipole-jump perturbation which accompanies the triplet-state excitation of chromophores having $\pi \to \pi^*$ or charge-transfer states such as xanthone dyes. Upon excitation, such molecules have been observed to relocate from hydrophobic, aggregated surfactant environments in their ground-states into the polar, hydrophilic solvent due to a large change in dipole moment. Our application of this concept would follow similar lines. Rose Bengal, Eosin Y, or other xanthone dye would be retained at a hydrophobic C18 or other alkylated silica surface and excited into its triplet state with a laser pulse. Time-resolved phosphorescence emission or excited state absorption (by diffuse reflectance) would be measured following laser excitation. The above probes are sufficiently long-lived to follow desorption kinetics at alkylated surfaces based on our initial laser temperature jump results from Berlin.

The final new area we plan to open up 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 which are not porous and yet have comparable specific surface areas as porous silica due to their small diameters, 50 to 100 Å. We have already developed some experience in handling colloidal silica samples, and have used them successfully in the laser temperature-jump experiments. Rapid mixing of particulate slurries or model silica compounds with reactive solutions will be possible by using a conventional stopped-flow apparatus which we recently adapted to fluorescence detection.

Personnel Supported on DOE Grant

Students who have been working on this project during the past year include: Scott Waite, graduate student who completed his Ph.D. during the summer; William Lacy, graduate student; Haibo Wang, graduate student; Lydia Olson, graduate student; Feiyan Ren, graduate student. During the past year, Scott Waite received an ACS Analytical Division Graduate Fellowship; Lydia Olson received partial support from a competitive NIH Graduate Traineeship.

Scientific Publications from DOE-Sponsored Research

1. "Electronic Spectroscopic Investigations of the Stationary Phase in Reversed Phase Liquid Chromatography", S. C. Rutan and J. M. Harris, J. Chromatogr. (in press, 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. (in press, 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. (submitted, in revision).

4. "Laser Temperature-Jump Investigation of Adsorption/Desorption Kinetics at Liquid/Solid Interfaces", S. W. Waite, J. Holzwarth, and J. M. Harris, J. Phys. Chem. (manuscript in preparation, 2nd Draft, copy available).

5. "Lateral Diffusion of Covalently-bound Siloxane Molecules on Silica Surfaces", H. Wang and J. M. Harris, J. Amer. Chem. Soc. (manuscript in preparation, 2nd Draft, copy available).

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. (manuscript in preparation, 1st Draft, copy available).

P.I. Invited Lectures Reporting DOE-Sponsored Research

1. "Multichannel Raman Spectroscopy for Investigation Chemical Reaction Kinetics", Symposium on Array Detectors in Spectroscopy, 1993 Pittsburgh Conference, Atlanta, March 10, 1993.

2. "Molecular Transport and Kinetics at Liquid/Solid Interfaces", Dayton Section SAS Meeting, Dayton, OH; April 22, 1993.

3. "Kinetics in Analytical Chemistry", Annual Summer Lecture Series, University of Wyoming, June 7 - 11, 1993

P.I. Invited Lectures Reporting DOE-Sponsored Research (continued)

4. "Molecular Transport and Kinetics at Liquid/Solid Interfaces", Occidental Chemistry Colloquium Lecture, SUNY Buffalo, November 5, 1993.

5. "Surface Binding, Heterogeneity, and Migration of Siloxane Ligands on Silica", Symposium on the Molecular Basis of Liquid Chromatography, 206th National ACS Meeting, Chicago, August 24, 1993.

Papers Contributed to Scientific Meetings Reporting DOE-Sponsored Research

1. "Direct Measurement of Sorption/Desorption Kinetics at a Reversed-Phase Chromatographic Silica Gel", S. W. Waite and J. M. Harris, 1993 Pittsburgh Conference, Atlanta, March 10, 1993.

2. "Temperature-jump Relaxation Kinetics at Liquid-Solid Interfaces: Joule Heating of Porous Silica and Direct Measurement of Sorption/Desorption Kinetics", S. W. Waite, J. M. Harris, and D. B. Marshall, 205th National ACS Meeting, Denver, April 1, 1993.

3. "Surface Binding and Migration of Siloxane Monolayers on Silica", H. Wang and J. M. Harris, XXth Annual FACSS Meeting, Detroit, October 21, 1993.

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