

AD-A202 436

4

DTIC ELECT. CORP.

OFFICE OF NAVAL RESEARCH

END-OF-CONTRACT-REPORT

for

Contract N00014-85-K-0712

R&T Code 413a005---02

Spectroscopic Studies of Fluid/Solid Interfaces

Joel M. Harris, Principal Investigator

Department of Chemistry
University of Utah
Salt Lake City, UT 84112

DTIC
ELECTE
DEC 02 1988
S D
E

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

* This document has been approved for public release and sale: its distribution is unlimited.

88 12 1 151

DESCRIPTION OF PROJECT

This program of research has been to develop spectroscopic methods for exploring chemical structure and molecular dynamics at interfaces between dielectric solids and liquids or supercritical fluids. The research was carried out using fluorescence and vibrational spectroscopy from probe molecules where spectral and temporal differences in emission, absorption, or scattering provide information about the surface onto which they are adsorbed or bound. Studies focused on the interfacial chemistry of silica and derivatized silica surfaces in contact with liquids and dense gases. The spectral response of probe molecules was used to observe differences in the chemical environment at the liquid-solid interface due to the presence of bound or adsorbed molecules. Fluorescence quenching can determine the distribution and transport of molecules at the interface. Time-resolution was found to be valuable in sorting out heterogeneous surface environments from differences in quenching rates of adsorbed or bound probe molecules. The dynamics of adsorption, desorption, and binding of molecules to solid surfaces were measured using perturbation methods. Concentration perturbations can be carried out on a time-scale of seconds. Fluorescence and Raman spectroscopy have begun to be modified to observe the perturbation of interfacial equilibria on time-scales as short as nanoseconds.

SIGNIFICANT RESULTS

The surface environment of C18, alkylated porous silica was studied as a function of overlaying solvent composition using the fluorescence vibronic fine structure of pyrene as an interfacial probe. The results indicated that the intercalation of organic constituents from the aqueous solution into the bonded layer produces an inverse relationship between the polarity of the C18 surface and that of the solution phase over a wide range of solvent compositions. In order to extend these experiments to fused silica (non-porous) surfaces, structural factors which control the reactivity of organosilane reagents to silica were identified using X-ray fluorescence and photoelectron spectroscopies.

The heterogeneity of alkylated silica surfaces was investigated by the effect of solution and surface quenching on the fluorescence of probe molecules. Correlation of these results with the fractal geometry of silica has been established through comparison measurements on flat, fused silica surfaces. Practical spin-offs of the spectroscopic methodology used in these studies was demonstrated for ultratrace-level detection and quantitation. The diffusion rates of quenching molecules near solid boundaries have also been measured to determine the extent of solvent structuring by the interface and its effect on its solvent properties. The development of vibrational methods, both Raman and infrared absorption, which are compatible with the silica substrate and solution conditions allowed us to make the first direct measurements of the rate of a siloxane binding reaction. We have reported the first direct measurements of the rates of siloxane binding reactions to oxide surfaces using ATR-FTIR methods. The inhibition of the reaction by an adsorbed

layer of reagent gives important information about increasing the efficiency of silane coupling reactions (used in composite materials and modified electrodes). Time-resolved, single-photon counting and noise analysis methods been refined to meet the requirements of measuring fluorescence from sub-monolayer coverage of probe molecules. Finally, the kinetics of a simple ionic reaction (metal ion decomplexation) at an interface has been measured indicating how charge interactions within the double-layer lead to inhomogeneous reaction rates.

The interfacial environments of alkylated silica surfaces were further studied by comparing fractal surface structures on porous silica with optically flat, fused silica using internal reflection fluorescence methods. Long-range order in ligands bound to flat silica is inferred. The mechanism of an unusual temperature-induced hysteresis in alkylated silica surfaces was also unraveled. The development of sensitive, surface spectroscopic methods: Raman, infrared, and real-time imaging reflectance, have led to three collaborative spectroelectrochemistry studies with Pons. We have made in-situ, Raman spectroscopic measurement of an adsorption isotherm at a liquid/solid interface. From a spectral analysis versus concentration, the vibrations of pyridine on silica show perturbations to the symmetric ring stretching mode but not the trigonal stretching mode. The conformation of the adsorbed pyridine thus inferred gives clues to its role as a catalyst in siloxane binding reactions.

PAPERS PUBLISHED IN REFEREED JOURNALS.

1. "Reactivity of Organosilane Reagents on Microparticulate Silica," M. L. Hunnicutt and J.M. Harris, *Anal. Chem.*, 54, 748 (1986).
2. "Fluorescence Studies of the Stationary Phase Chemical Environment in Reversed-Phase Liquid Chromatography," J. W. Carr and J. M. Harris, *Anal. Chem.*, 58, 626 (1986).
3. "Heterogeneity of Reversed-Phase Chromatographic Surfaces: Quenching of Sorbed Pyrene Fluorescence", J. W. Carr and J. M. Harris, *Anal. Chem.* 59, 2546 (1987).
4. "In-Situ Fluorescence Detection of Polycyclic Aromatic Hydrocarbons Following Preconcentration on Alkylated Silica Adsorbents", J. W. Carr and J. M. Harris, *Anal. Chem.* 60, 698 (1988).
5. "Attenuated Total Reflectance FT-IR Spectroscopy to Measure Interfacial Reaction Kinetics at Silica Surfaces", D. B. Parry and J. M. Harris, *Appl. Spectrosc.* 42, 997 (1988).
6. "A Conducting Polymer Formed from the Anodic Oxidation of Toluene in Acetonitrile", K. Ashley, D. B. Parry, J. M. Harris, and S. Pons, *J. Chem. Soc., Chem. Commun.* 1253 (1988).

PAPERS SUBMITTED OR ACCEPTED IN REFEREED JOURNALS.

1. "Properties of Electrochemically Generated Poly(p-Phenylene)", K. Ashley, D. B. Parry, J. M. Harris, and S. Pons, *Electrochim. Acta* (in press, 1988).
2. "Total Internal Reflection Fluorescence for Adsorbed Probe Molecules Studies of Liquid/Solid Interfacial Environments", K. C. Hartner, J. W. Carr, and J. M. Harris, *Appl. Spectrosc.* (in press, 1989).
3. "The Behavior of Disk Electrodes: Optical Imaging of the Concentration Distribution over a Disk Electrode under Galvanostatic Conditions", J. Daschbach, S. F. Simpson, J. M. Harris, M. Fleischmann, and S. Pons, *J. Electroanal.* (in press, 1988).
4. "Temperature-Induced Changes in Reversed-Phase Chromatographic Surfaces: C8 and C9 Polymeric Ligands", J. W. Carr and J. M. Harris, *J. Chromatogr.* (submitted for publication).
5. "In Situ Fluorescence Studies of Aluminum Ion Complexation by 8-Hydroxyquinoline Covalently Bound to Silica", M. R. Weaver and J. M. Harris, *Anal. Chem.* (submitted for publication).
6. "Modification of Quartz Surfaces via Thiol-Disulfide Interchange", J. K. Yee, D. B. Parry, K. D. Caldwell, and J. M. Harris., *Langmuir* (submitted for publication).

INVITED PRESENTATIONS AT MEETINGS OF SCIENTIFIC SOCIETIES AND SEMINARS.

1. "Spectroscopic Studies of the Silica/Solution Interface: Application to Optical Sensors," Symposium on "Fiber-Optic Sensors," 168th Meeting of the Electrochemical Society, Las Vegas, October 16, 1985.
2. "Fluorescence Studies of Liquid/Solid Interfaces," Physical Chemistry Seminar, University of California, Berkeley, October 29, 1985.
3. "Fluorescence Studies of the Liquid/Solid Interface," Department of Chemistry Seminar, University of Alabama, November 20, 1985.
4. "Application of Flow Injection Methods to Ultra-Trace Level Spectroscopic Determinations," Pittsburgh Conference, Atlantic City, March 13, 1986.
5. "Advances in Regression: Getting the Most from Least Squares," 191st ACS National Meeting, New York, April 17, 1986.
6. "Multichannel Detection and Resolution of Overlapped Chromatographic Peaks," 39th Annual ACS Analytical Summer Symposium, Salt Lake City, June 20, 1986.

7. "Information Processing in Analytical and Physical Chemistry," Two-Week Short Course, Department of Chemistry, University of California, Berkeley, September 8-19, 1986.
8. "Multichannel Detection and Resolution of Overlapping Chromatographic Peaks", Millipore Corporation, Waters Division, Milford, Mass., September 29, 1986.
9. "Fluorescence Spectroscopic Studies of Liquid/Solid Interfaces", Naval Research Laboratories, Washington, DC, December 11, 1986.
10. "Time-Resolved Fluorescence Studies of Molecular Interactions at Reversed-Phase Silica Surfaces", Pittsburgh Conf., Atlantic City, March 11, 1987.
11. "Chemical Kinetics at Liquid/Solid Interfaces", Procter and Gamble, Miami Valley Laboratories, March 17, 1987.
12. "Time Resolution as a Focus in Spectroscopic Instrumentation", 193rd National ACS Meeting, Denver, April 7, 1987.
13. "Time-Resolved Fluorescence Studies of Molecular Interactions at Reversed-Phase Silica Surfaces", 193rd National ACS Meeting, Denver, April 8, 1987.
14. "Squeezing Information Out of Hyphenated Analytical Data", Syracuse ACS Section Meeting, Syracuse University, May 12, 1987.
15. "Harmony from Dissonance: When Noise Provides Time-Resolved Chemical Information", Binghamton ACS Section Meeting, SUNY Binghamton, May 13, 1987.
16. "Harmony from Dissonance: When Noise Provides Time-Resolved Chemical Information", Monmouth County ACS Section Meeting, Union Beach, NJ, May 14, 1987.
17. "Flow Injection and In Situ Fluorescence Detection of Analytes on Derivatized Silica Surfaces", Dow Chemical, Freeport, October 15, 1987.
18. "Advances in Regression: Use of Models in Analytical Spectroscopic Data Analysis", 2nd Hidden Peak Symposium on Computer-Enhanced Analytical Spectroscopy, Snowbird, June 1, 1988.
19. "Advances in Regression: Getting the Most from Least Squares", 1988 E. H. Boomer Memorial Lecture Series, University of Alberta, May 18, 1988.
20. "Time-Resolved Spectroscopy at Liquid/Solid Interfaces", 1988 E. H. Boomer Memorial Lecture Series, University of Alberta, May 19, 1988.
21. "Spectroscopic Studies of Liquid/Solid Interfaces", 3rd Chemical Congress of North America and 195th National ACS Meeting, Toronto, June 9, 1988.

CONTRIBUTED PRESENTATIONS AT MEETINGS OF SCIENTIFIC SOCIETIES.

1. "Fluorescence Studies of Adsorbed Molecules in Reversed-Phase Chromatographic Systems," with J. W. Carr, Pittsburgh Conference, Atlantic City, March 13, 1986.
2. "Fluorescence Studies of Molecular Interactions at Reversed-Phase Silica Surfaces" with M. L. Hunnicutt and J. W. Carr, 10th International Symposium on Column Liquid Chromatography, San Francisco, May 22, 1986.
3. "In Situ Fluorescence Studies of Metal Chelates Covalently Bound to Silica" with M. R. Weaver, 13th Annual FACSS Meeting, St. Louis, September 30, 1986.
4. "Holographic Relaxation Measurements of Diffusion in Supercritical Fluids", with X.-R. Zhu, postdeadline contribution to ARO/ONR Workshop on Supercritical Fluid Technologies, May 7, 1987.

GRADUATE STUDENTS AND POSTDOCTORAL FELLOWS SUPPORTED BY CONTRACT

Postdocs:

Dr. Stan Simpson, Ph. D. from University of Kentucky
Dr. Carol Korzeniewski, Ph. D. from University of Utah

Graduate Students:

Mr. Michael Weaver, B.S. from Northern Arizona University
Mr. Andy Wong, B.S. from University of Idaho
Ms. Diane Parry, B.S. from University of Cincinnati
Mr. Ken Hartner, B.S. from Wayne State University
Ms. Carol Rabke, B.S. from Randolph-Macon College



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	