AD-A159 529 STUDY OF SYNCHROTRON RADIATION FROM WET ELECTRODE SURFACES(U) IBM RESEARCH LAB SAN JOSE CA L BLUM ET AL. 30 SEP 85 N00014-81-C-0776 1/1

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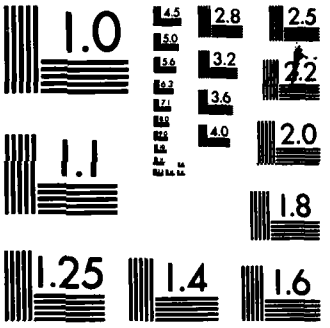

MICROCOPY RESOLUTION TEST CHART
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OFFICE OF NAVAL RESEARCH

PUBLICATIONS / PATENTS / PRESENTATIONS / HONORS REPORT

for

1 October 1984 through 30 September 1985

for

OFFICE OF NAVAL RESEARCH
CONTRACT N0014-C-0776
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STUDY OF SYNCHROTRON RADIATION FROM WET ELECTRODE SURFACES

PRINCIPAL INVESTIGATORS:

Dr. Lesser Blum: Physics Department
Faculty of Natural Sciences
University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Dr. Joseph G. Gordon II: IBM San Jose Research Laboratory
D/K34, B/028-1
5600 Cottle Road
San Jose, California 95193

Part I.

A. Papers Submitted

1. Fluorescence Detected Surface EXAFS (FDSEXAFS) of Iodine on Platinum: *In Situ* Structural Characterization of an Electrochemical Interface.

   J. G. Gordon, O. R. Melroy, G. L. Borges, D. L. Reisner, H. D. Abruna, P. Chaudrasekhar and L. Blum

   J. Am. Chem. Soc.

2. Discrete Site Adsorption: An Exactly Solvable Model of a Coulomb system in Two Dimensions and Some General Relations.

   M. L. Rosinberg, L. Blum and J. L. Lebowitz

   J. Chem. Phys.

3. Analytic Solution of the Molecular Ornstein-Zernike Equation for Non-spherical Molecules: Spheres with Anisotropic Surface Adhesion.

   P. T. Cummings and L. Blum

   J. Chem. Phys.

4. An Improved Closure of the Born-Green-Yvon Equation for the Electric Double Layer.

   L. Blum, C. Caccamo and G. Pizzimenti

   J. Phys. Chem.

B. Papers Published in Refereed Journals

"An Exactly Solvable Model for Ideally Polarizable Interfaces," M. L. Rosinberg and L. Blum, Chem. Phys. Letters 106, 48 (1984).

"The Ideally Polarizable Interface: A Solvable Model and Sum Rules," M. L. Rosinberg and L. Blum, J. Chem. Phys. 81 3700 (1984).

"The Ideally Polarizable Interface: Integral Equations," M. L. Rosinberg, L. Blum and J. L. Lebowitz, J. Chem. Phys. 83 892 (1985).

"Statistical Mechanics of Ion-dipole Mixtures: On Exactly Solvable Model in One Dimension," F. Vericat and L. Blum, J. Chem. Phys., 82 1492 (1985).

"An Improved Approximation for the Primitive Model of the Electric Double Layer," C. Caccamo, G. Pizzimenti and L. Blum, Chem. Phys: Liquids, 14 311 (1985).

C. Books in Print

The Electric Double Layer - A Comprehensive Approach, L. Blum, in "Fluid Interfacial Phenomena," C. A. Croxton, editor; J. Wiley, Publisher.

D. Books Published

No books published.

E-F. Patents

No patents filed or granted.

G. Invited conferences

L. Blum, The Electric Double Layer
University of Southampton, Sept. 30, 1984

L. Blum, Analytic Studies of the Electric Double Layer
NBS Gaithersburg, June 10, 1985

J. Gordon, "Weighing the Electrode Surface - The Oscillating Quartz Microbalance," Gordon conference on electrochemistry, Santa Barbara, CA, January 20, 1985.

Part II

A. Funding History

October 1, 1981 - September 30, 1982 --- $115,551
October 1, 1982 - September 30, 1983 --- $118,366
October 1, 1983 - October 15, 1984 --- $85,498
October 1, 1984 - September 30. 1985 --- $130,008

B. Current Telephone Numbers

Lesser Blum (809) 763-3390
Joseph Gordon (408) 256-1266

C. Description

The purpose of the project is to probe the structure of the charged liquid:solid interface using synchrotron radiation. The initial experiment is to measure the EXAFS spectrum of a halide on a flat metallic electrode surface. By obtaining the EXAFS spectrum as a function of potential, we should be able to determine the extent of adsorption and how the surface structure changes with coverage. In addition, the theory of progressively more realistic models of the charged interface is being studied:

1. A rather exhaustive study of the so called primitive model, using the Bron-Green-Yvon equation and accurate bulk correlation functions.

2. A model for the structure of water with sticky-directional forces is proposed. This model has the correct structure of liquid water and should be more realistic than hard spheres with point dipoles.

3. A model of the charged interface with discrete adsorption sites: In particular, we can solve exactly the one component plasma in two dimensions.

D. Results

Experiment

During 1984-85, we had one run a the Cornell High Energy Synchrotron Source (CHESS) and, taking advantage of the high energy radiation available at CHESS, studied the adsorption of Iodine on Platinum. Using a grazing incidence geometry and fluorescence detection, surface EXAFS of a monolayer of iodine adsorbed on Platinum (111) single crystals was detected. Although the near edge structure was rather noisy, it produced a clearly resolved peak in the Fourier transofrmed corresponding to an I-Pt distance of ~ 2.5 Å. (This is a preliminary distance subject revision upon further refinements.) These results demonstrate the feasibility of *in situ* structural study of electrochemical interfaces using EXAFS.

Theory

In collaboration with the group at Messina, we performed extensive calculations to test the Born-Green-Yvon theory for the primitive (continuum dielectric solvent). We used the most accurate bulk pair correlation functions available, and got very good agreement with computer simulations at high concentrations (up to 2M). For concentrations up to 4M we observe charge layering effects near the electrode walls.

A model with a hard core, a point dipole and a sticky interaction of water was studied. This model reproduces the nearest neighbor, structure of liquid water, and was solved analytically in the Perius - Yevick approximation.

Finally we have also studied a model with sticky lattice sites, which mimics a realistic surface. Exact contact relations can be derived for the average adsorbed density. A two dimensional model has also been solved exactly.

E. Summary of Plans

Experiment

We expect run again at CHESS in November '85 and summer '86 when we will acquire better EXAFS data on the I-Pt system and also examine I on Ag. Beam time will be requested from SSRL (Stanford) for a run in spring '86 to re-examine Br and Pb on Ag. (Competition for beam time at SSRL is intense because of the reduced running schedule which has resulted from their budgetary restrictions.) We also hope to schedule a grazing incidence x-ray diffraction experiment at SSRL or Brookhaven in 1986, in collaboration with groups from LBL or Oak Ridge, respectively.

Theory

We will pursue our effort to get a simple, yet accurate equation for the primitive model which could be used for the ion-dipole mixture and also for the more advanced sticky models.

We intend also to address the problem of the polarizable membrane in which one of the sides is a quantum mechanical system (jellium).

F. Graduate Students

For the next year, two graduate students will participate in the project.

1. Mr. Samuel Torres
2. Mr. Manuel Quijada

Post-doctorals

We expect one post-doc, as yet unknown, to participate.

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