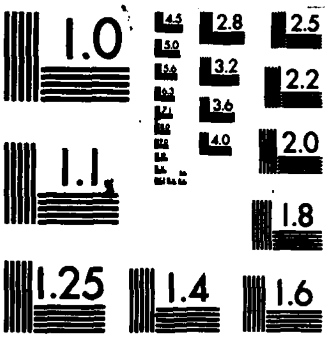
AD-A137 892 FINAL TECHNICAL REPORT OF RESEARCH PERFORMED UNDER 1/1
GRANT AFOSR-80-0262(U) GEORGETOWN UNIV WASHINGTON D C
R DE LEVIE 1983 AFOSR-TR-84-0092 AFOSR-80-0262

UNCLASSIFIED F/G 7/4 NL

END
FILMED
3-84
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ADA137892

unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

JAN

10

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FOR

1. REPORT NUMBER
AFOSR-TR- 84-0092

2. GOVT ACCESSION NO

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
FINAL TECHNICAL REPORT OF RESEARCH PERFORMED UNDER Grant AFOSR-80-0262

5. TYPE OF REPORT & PERIOD COVERED
Final Report 9/80-10/83

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
Robert de Levie

8. CONTRACT OR GRANT NUMBER(s)
AFOSR-80-0262

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Georgetown University
Washington D.C. 20057

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
61102F
2303/A1

11. CONTROLLING OFFICE NAME AND ADDRESS
Air Force Office of Scientific Research/
NC, Building 410, Bolling AFB, D.C. 20332

12. REPORT DATE
1983

13. NUMBER OF PAGES
6

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report)
unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Final report

DTIC
ELECTE
FEB 13 1984
S D

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes the research accomplished during the report period, and compares it with the original objectives, which were more than met.

DTIC FILE COPY

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

84 02 10 083

AFOSR-TR- 84-0092

FINAL TECHNICAL REPORT OF RESEARCH
PERFORMED UNDER AFOSR GRANT 80-0262

Summary. The original objective of this project was, first, to study the effect of adsorbed ions on the electrosorption of organic molecules and vice versa and, secondly, to study the kinetics of formation of condensed films. The first objective was achieved, although the results obtained were rather unexpected; the second objective was met far beyond our original hope, as it proved possible to develop an entirely new approach to the general problem of nucleation and growth. This work is continuing.

Study of the mutual effects of adsorbed ions and molecules. Numerous reports in the literature had suggested that there was a strong effect of specifically adsorbed anions on the simultaneous adsorption of organic molecules and, likewise, of organic electrosorption on the specific adsorption of anions. Such conclusions had often been reached by fitting measured adsorption data to presumed adsorption isotherms, followed by an interpretation of the fitted parameters. This method clearly depends on the validity of the assumed isotherm about which, unfortunately, there is a significant lack of consensus. We therefore set out to investigate the presence or absence of such mutual interactions without making any model assumptions. The choice of systems to study was limited by the following considerations:

a. There should be a significant range of potentials over which adsorption of both ions and organic molecules should occur simultaneously. Since ion adsorption is most pronounced at highly charged interfaces, whereas adsorption of neutral molecules is maximal in the region of zero electrode charge, such a requirement of sufficient adsorption overlap restricts the choice to strongly adsorbed ions and molecules.

b. The system should be one for which the thermodynamic activities of the mixtures are known, so that the interfacial effects can clearly be distinguished from those due to bulk interactions.

Only few systems satisfy both requirements, and we have settled on one of these, viz. the coadsorption of NaCl and sucrose. A large number of surface tension data (approximately 30,000) were collected with our computer-controlled, high-precision instrument. The results were surprising: after correction for the considerable mutual interactions in the bulk solution, and upon comparing data at constant electrode charge density (which already incorporates some effects of ionic and organic adsorption), no significant mutual effects could be detected. This despite the fact that chloride ions and sucrose molecules are considerably more crowded on the interface than they are in the bulk solution. Our tentative interpretation of this result is that the mutual effects of NaCl and sucrose are most likely to be indirect, through their influence on the water structure. Since the structure of interfacial water is likely to be determined largely by the electric field, the influence of adsorbed ions and molecules on that structure, and hence their mutual interaction, may well be much weaker than that in solution.

Study of the kinetics of formation of condensed films.

When we began this project, a number of intriguing observations had been reported, showing that condensed monolayer films could be formed from a variety of organic molecules and under quite a range of circumstances. In many cases, their rate of formation had been reported to be quite slow, so that the kinetics of their formation should be experimentally accessible.

We first established that the formation of these films could be described in terms of conventional models for nucleation and growth of two-dimensional layers. Such models, however, allow only a semi-quantitative description, because they do not provide a way to differentiate between the rate parameters for nucleation and those for growth, even though these can be expected to have quite different functional behaviors.

We realized that, in order to make progress beyond this point, a radically new approach was needed, which would allow us to observe individual nucleation events. Guided by our earlier work with bilayer membranes, where such observations are sometimes possible when the membrane area is made sufficiently small, we tried the same approach here, and were successful. On a sufficiently small electrode, we are now able to observe individual nucleation events and, separately, the kinetics of growth of single nuclei.

Since individual nucleation events are stochastic, i.e., randomly distributed around some mean value, a large number of observations needs to be recorded in order to extract from these the rate parameters of nucleation. We have therefore designed and built the necessary automated equipment, and developed the required data analysis methods, for such a stochastic analysis. Our principal findings so far can be summarized as follows:

a. The formation of condensed films of thymine and of guanine at the interface between mercury and aqueous electrolyte solutions is a nucleated process.
b. Such nucleation can be observed as a stochastic process, by making the electrode surface sufficiently small. In our case, an electrode area of approximately 0.04 mm^2 was used.
c. Nucleation in both cases follows non-steady-state kinetics; the corresponding statistics are those of a non-homogeneous Poisson distribution.
d. The rate of nucleation is a strong function of potential. The specific law involved has yet to be determined.
e. From the nucleation statistics, one can obtain an estimate of the stoichiometry of the critical nucleus. The numbers so obtained, of the order of 10, also depend on potential.
f. Growth of single nuclei can be observed directly. Such growth can be described quantitatively by a simple model of isotropic growth.
g. The resolution of our growth data is insufficient to decide whether the condensed film is a two-dimensional liquid or solid, i.e., whether its shape is principally determined by considerations of edge energy or those of molecular packing.
h. The dissolution of a condensed film follows simple first-order order kinetics, and does not seem to involve nucleation.

j. With thymine, additional condensed phases are obsereved at lower temperatures. It is likely that these are also monolayer films, but with different molecular orientations, governed largely by interactions of the dipole moment with the electric field of the double layer.

k. The region of stability of the condensed phases observed depends strongly on both potential and concentration, as expected. However, it also depends on the nature and concentration of the electrolyte used, although the precise nature of that dependence has not yet been clarified.

Clearly, the possibility to observe, separately, the kinetics of nucleation and growth, and to study their functional dependencies, is opening a rich new field of observations in an area of general importance in many scientific disciplines. The type of detailed information on the kinetics of nucleation and growth which we can now obtain is available in only very few cases. Our electrochemical context is very helpful, because the two-dimensional nature of the phenomenon allows precise control of experimental conditions as well as efficient buffering of interfacial concentrations while, at the same time, sensitive detection is facilitated.

Related studies.

In parallel studies we have investigated a number of aspects of ac and dc polarography. We have devised and tested a simple alternative to Fourier transform ac polarography, and are now testing an extension of dc polarography to make it more sensitive Our continued involvement in the refinement of electrochemical instrumentation has, of course, helped greatly in our studies of film formation, where we monitor the change of interfacial capacitance with time by ac polarography.

We have also completed detailed theoretical studies of nucleation and of one-dimensional growth. The nucleation studies resulted in the above-mentioned method to determine the stoichiometry of the critical nucleus.

Publications.

1. "Double layer capacitance measurements with digital synchronous detection at a dropping mercury electrode", P. F. Seelig and R. de Levie, Anal. Chem., 52, 1506 (1980).

2. "Sampling error in Fourier and Hadamard transform capacitance measurements", R. de Levie, Anal. Chem., 52, 1535 (1980).

3. "On the admittance of lipid bilayer membranes II: uncouplers and ion carriers", R. de Levie and P. F. Seelig, J. Electroanal. Chem., 117, 167 (1981).

4. "The structure of charged interfaces", R. de Levie, Sensors and Actuators, 1, 97 (1981).

5. "Some aspects of modern electrochemical instrumentation", R. de Levie, Trans. SAEST, 109 (1981).

6. "On the mutual interactions of adsorbed molecules and ions: sucrose and chloride in the ternary system H_2O + sucrose + NaCl at the mercury-water interface", M. Krishnan and R. de Levie, J. Electroanal. Chem., 131, 97 (1982).

7. "Stochastic effects in the formation of condensed thymine films at the water-mercury interface", R. Sridharan and R. de Levie, J. Phys. Chem., 86, 4489 (1982).

8. "Hadamard transform alternating current polarography", C. C. Chang and R. de Levie, Anal. Chem., 55, 356 (1983).

9. "Closoborane anion adsorbs onto lipid bilayer membranes and affects ion transport", R. J. Atwell and R. de Levie, J. Electroanal. Chem., 148, 305 (1983).

10. "On one-dimensional nucleation and growth of "living" polymers I: homogeneous nucleation", M. P. Firestone, S. K. Rangarajan and R. R. de Levie, J. Theoret. Biol., in press.

11. "On one-dimensional nucleation and growth of "living" polymers II: Growth at constant monomer concentration", S. K. Rangarajan and R. de Levie, J. Theoret. Biol., in press.

12. "Electrochemical observations of single molecular events", R. de Levie, Advances in Electrochemistry and Electrochemical Engineering, H. Gerischer and C. W. Tobias, eds, Wiley, in press.

13. "On the statistics of electrochemical nucleation: application of the non-homogeneous Poisson distribution", R. Sridharan and R. de Levie, J. Electroanal. Chem., submitted.

14. "A simple separation of Faradaic and charging polarographic currents", R. J. Atwell and R. de Levie, in preparation.

15. "The kinetics of formation of thymine films at the mercury-water interface I: deterministic observations", R. Sridharan and R. de Levie, in preparation.

16. "The kinetics of formation of thymine films at the mercury-water interface II: stochastic observations", R. Sridharan and R. de Levie, in preparation.