

2

(U)

SECURITY CLASSIFICATION

AD-A236 916



ON PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Final report		7a. NAME OF MONITORING ORGANIZATION Office of sponsored projects Northern Illinois University	
5a. NAME OF PERFORMING ORGANIZATION Department of Chemistry Northern Illinois University	6a. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code) DeKalb, Illinois 60115	
6b. ADDRESS (City, State, and ZIP Code) DeKalb, Illinois 60115		8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research	
8b. OFFICE SYMBOL (If applicable) ONR		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-8-K0075	
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-0000		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 6115N	PROJECT NO. RR04108
		TASK NO. 441K	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Investigation of the interface between two immiscible electrolytes applied to membrane electrochemistry (U).			
12. PERSONAL AUTHOR(S) Petr Vanysek			
13a. TYPE OF REPORT FINAL	13b. TIME COVERED FROM 88-10-6 TO 91-04-15	14. DATE OF REPORT (Year, Month, Day) 91-5-18	15. PAGE COUNT 10
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		MEMBRANE ELECTROCHEMISTRY, IONIC, CHANNELS, IMMISCIBLE electrolytes, MICROINTERFACES, PHYSICAL ELECTROCHEMISTRY	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
The final report sums the work done on immiscible electrolyte solutions and their interfaces during the duration of the contract. Two categories of findings are presented: instrumentation development and modification, and inquiry into new physical principles. New instrumentation includes: Automated apparatus for impedance measurement, apparatus for work on microinterfaces, apparatus for light beam deflection studies, apparatus for impedance determination from analysis of noise signal. New findings include: Study on potential sensitive fluorescent dyes, study of adsorption of proteins on water/nitrobenzene interfaces, development of microinterface as a model of channel transport and as an analytical probe, studies of ion transport in ion exchange membrane structure.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION (U)	
22a. NAME OF RESPONSIBLE INDIVIDUAL Petr Vanysek		22b. TELEPHONE (Include Area Code) 815/753-6876	22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH
FINAL REPORT

for

Contract # N00014-88-K0075

R&T Code 413k001

Investigation of the interface between two immiscible electrolytes
applied to membrane electrochemistry

Petr Vanýsek

Northern Illinois University

Department of Chemistry
DeKalb, IL 60115

18 May 1990

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.

Annotation For	
ADAMS CRAM1	☒
DISPATCH	☐
CHANGING BOARD	☐
Justification	
by	
DISPATCH	
Availability	
Availability	
Region	
A-1	



91 6 6 070

91-01432

The purpose of the work was to investigate various aspects of electrochemical and electrical behavior of interfaces between two immiscible solutions of electrolytes. The interface has some properties similar to those of metal electrodes. Therefore, methodology known from the work with metal electrodes ("classical electrochemistry") can be applied to these studies in many cases. More importantly, the interface also represent, in a model simplified way, the potential/ionic distribution encountered on biological membranes. the scope of the work was to learn about the processes occurring on such interfaces and to find pertinent links between such interfaces and membrane electrochemistry.

The progress and the results of three years of work based on Contract # N00014-88-K0075 were continuously documented by regular submission of Technical Reports. Overall, 39 reports were filed (see appendix). Most significantly, the results of the work were also published as refereed publications (14). Two more publications are currently pending and more work at various stages is under way. This further research initiative is carried out under new ONR contract, # N00014-91-J-1058.

The work of the past 3 years in our laboratory can be divided into two parts; development of new techniques and approaches to tackle to problems of polarized interface between two immiscible electrolytes, and second; search for and investigation of new principles and systems, associated with the very physical nature of the polarized interfaces. Although the two parts are related and often carried out by the same researcher, for summary purposes they can be better appreciated if treated separately.

The major component of our work involves the study of impedance of the interfaces between the two immiscible phases. In the early stages the measurement was done by a point-by-point approach. Inasmuch the instrumentation is capable of computer interfacing, we have developed programs that allow automated data gathering and retrieval. Our latest addition to the software part was writing a program that allows automated impedance measurements at preprogrammed bias interfacial potentials. Such technique is essential for large scale evaluations of many systems. Point-by-point approach is in this case inadequate. Not only the demand on operator's time would be unreasonable, but also the chances of error during this work would be rather high. The raw impedance data are finally being evaluated by available nonlinear least square fitting routines. These programs were either purchased or obtained through collaboration.

Although impedance techniques are the approach of choice in our laboratory, we have also developed several experimental work stations allowing voltammetric measurements. In particular we had to develop or modify instrumentation which would allow work at low currents experienced with our microinterfaces. For that low current amplifiers equipped with appropriate shielding boxes were constructed. Great deal of time was spent to achieve optimal response with minimal extraneous noise interference.

As a totally new instrumental approach in electrochemistry of liquid/liquid interfaces was constructing an apparatus evaluating impedance of the electrochemical system based on the analysis of power spectrum of the studied system originating from thermal noise of the inherent resistances of the system. The original idea arose from collaborative efforts; since then we have developed a system which can be supported through an interface of an ordinary IBM compatible PC. The research based on this technique, including learning of the methodology is currently under way.

Finding of new physical principles and phenomena were also documented in our technical reports and published works. Chronologically first was the work that involved studies of fluorescent dyes used in mapping potential differences on biological membranes. Ion our work we studied fluorescence changes of so called slow dyes (oxacyanines) on the

interface between water and nitrobenzene as a function of varying interfacial potential. We have shown, both experimentally and theoretically the importance of presence of excess of salts in the system. This requirement has not been until now understood or fully appreciated, presumably also because in biological systems there are some salts inherently present.

Other work involved studies of adsorption on liquid/liquid interfaces. In particular, we have investigated behavior of adsorbed bovine serum albumin on water/nitrobenzene interface. The comprehensive study based on impedance measurements was carried out at varied protein concentration, pH, temperature and applied interfacial potential. Semiautomated impedance taking allowed determination of such parameters as critical protein concentration for monolayer thickness and determination of isoelectric points and potentials of zero charge.

Very significant was our contribution to development of new probe in liquid/liquid electrochemistry, the microinterface. The microinterface follows the ideas of microelectrodes in that the diffusion control at the minute interfaces is hemispherical, decreasing thus contribution of resistance drop during current-voltage measurements. This enables work in more resistive systems. The microinterface can be also utilized in work related to channel studies. When forming the interface in a longer capillary tube, a situation similar to a channel or pore is created. Although the contribution of the resistance of the microinterface to voltammetric distortion is negligible, the absolute resistance of such a system is inherently high. This has been advantageous in employing this system in noise analysis. Thermal noise generated by a system is proportional to resistance of the system. Therefore, any practical signals can be obtained only from systems that have resistance of approximately a megaohm or higher. Microinterfaces are thus genuinely suited for such experimental approach.

The work, as a research on new initiative, has proven extremely successful. the phenomena associated with electrochemistry on L/L interfaces have caught attention of the scientific community. Increased number of publications related to these problems appears every year and international symposia on this subject are being organized. The support of this area by the ONR contract has firmly placed roots and background of this discipline in the USA.

APPENDIX

List of technical reports:

ONR Technical Report No. 001: Deborah H. Wiegand and Petr Vanýsek: Distribution of oxacyanine dyes between water and nitrobenzene: Determination of the partition constants, association and potentials of transfer of the dye cations on liquid/liquid interfaces. Accepted manuscript. 12 October 1989.

ONR Technical Report No. 002: Zhisheng Sun and Petr Vanýsek: Electrochemical determination of lead and lead ion transfer at liquid/liquid interfaces. Accepted manuscript. 12 October 1989.

ONR Technical Report No. 003: Petr Vanýsek: Impedance spectroscopy and impedance related problems in electrochemistry on the interface between two immiscible electrolytes. Submitted manuscript. 12 October 1989.

ONR Technical Report No. 004: Petr Vanýsek and Irma C. Hernandez: Electrochemical behavior of a microscopic interface between two immiscible electrolytes. Submitted manuscript. 12 October 1989.

ONR Technical Report No. 005: Petr Vanýsek and Zhisheng Sun: Bovine serum albumin adsorption on a water/nitrobenzene interface. Submitted manuscript. 12 October 1989.

ONR Technical Report No. 006: Petr Vanýsek: Uncertainty in the potential of a reference interface in liquid/liquid measurements. Submitted manuscript. 12 October 1989.

ONR Technical Report No. 007: Petr Vanýsek and Jianjiang Xu: Solidified microinterface between two immiscible electrolytes: Transfer of picrate and tetramethylammonium ions across a gel/liquid interface. Submitted manuscript. 26 October 1989.

ONR Technical Report No. 008: Petr Vanýsek, Irma C. Hernandez and Jianjiang Xu: Supporting electrolytes for electrochemistry on liquid/liquid interfaces: Crystal violet and tetrabutylammonium tetraphenylborate in nitrobenzene. Submitted manuscript. 18 December 1989.

ONR Technical Report No. 009: Deborah H. Wiegand and Petr Vanýsek: Distribution of oxacyanine dyes between water and nitrobenzene: Determination of the partition constants, association and potentials of transfer of the dye cations. Corrected proofs of a manuscript. 18 December 1989.

ONR Technical Report No. 010: Irma C. Hernandez: Investigation of transport behavior of semihydrophobic ions across a microscopic interface formed between nitrobenzene and water. Defended M.S. thesis. 18 December 1989.

ONR Technical Report No. 011: Petr Vanýsek and Zhisheng Sun: Bovine serum albumin adsorption on a water/nitrobenzene interface. Corrected manuscript, accepted by the journal. 18 December 1989.

ONR Technical Report No. 012: Petr Vanýsek and Irma C. Hernandez: Ion transport across a microscopic interface between two immiscible electrolytes.

Submitted manuscript. 8 January 1990.

ONR Technichal Report No. 013: Petr Vanýsek: Analytical applications of electrochemical processes on the interface between two immiscible electrolyte solutions. Draft manuscript. 8 January 1990.

ONR Technichal Report No. 014: Petr Vanýsek: Uncertainty in the potential of a reference interface in liquid/liquid measurements. Corrected galley proofs. 8 January 1990.

ONR Technichal Report No. 015: Petr Vanýsek, Irma C. Hernandez and Jianjiang Xu: Determination of choline, picrate, dodecylsulfate and several quaternary ammonium salts on an electrified liquid/liquid microinterface. Submitted manuscript. 10 January 1990.

ONR Technichal Report No. 016: Deborah H. Wiegand and Petr Vanýsek: Potentiometry on the water/nitrobenzene interface in the presence of oxacyanine dyes. Submitted manuscript. 10 January 1990.

ONR Technichal Report No. 017: Petr Vanýsek and Richard P. Buck: Multi-ion Nernst distribution potential equations: Interfacial potentials at equilibrium liquid/liquid and membrane interfaces. Submitted manuscript. 22 February 1990.

ONR Technichal Report No. 018: Deborah H. Wiegand and Petr Vanýsek: Distribution of oxacyanine dyes between water and nitrobenzene: Determination of the partition constants, association and potentials of transfer of the dye cations on liquid/liquid interface. Reprint from J. Colloid. Interface. Sci. 135, 272–282 (1990). 22 February 1990.

ONR Technichal Report No. 019: Petr Vanýsek and Zhisheng Sun: Bovine serum albumin adsorption on a water/nitrobenzene interface. Corrected galley proofs. 4 March 1990.

ONR Technichal Report No. 020: Richard P. Buck and Petr Vanýsek: Interfacial potential difference at mixed conductor interfaces: Nernst, Nernst–Donnan, Nernst distribution and generalizations. Submitted manuscript. 5 March 1990.

ONR Technichal Report No. 021: Zhisheng Sun and Petr Vanýsek: Electrochemical determination of lead and lead ion transfer at liquid–liquid interfaes. Reprint from Anal. Chim. Acta 228, 241–249 (1990). 11 March 1990.

ONR Technichal Report No. 022: Petr Vanýsek and Irma C. Hernandez: Ion transport across a microscopic interface between two immiscible electrolytes. Revised manuscript. 22 March 1990.

ONR Technichal Report No. 023: Petr Vanýsek and Irma C. Hernandez: Microscopic interface between two immiscible electrolytes: A parallelism to an ultramicroelectrode. Accepted manuscript. March 1990.

ONR Technichal Report No. 024: Petr Vanýsek, Irma C. Hernandez and Jianjiang Xu: Supporting electrolytes for electrochemistry at liquid/liquid interfaces: Crystal violet and tetrabutylammonium tetraphenylborate in nitrobenzene. Accepted manuscript. March 1990.

ONR Technichal Report No. 025: Deborah H. Wiegand: Thermodynamics of the transport of oxacyanine dyes across the water/nitrobenzene interface. Defended PhD. dissertation. March 1990.

ONR Technichal Report No. 026: Petr Vanýsek: Impedance spectroscopy and impedance related problems in electrochemistry on the interface between two immiscible electrolytes. Reprint from *Chimicaoggi* **8**, 47–53 (1990). April 1990.

ONR Technichal Report No. 027: Petr Vanýsek and Zhisheng Sun: Bovine serum albumin adsorption on a water/nitrobenzene interface. Reprint from *Bioelectrochem. Bioenerg.* **23**, 177–194 (1990). 22 June 1990.

ONR Technichal Report No. 028: Petr Vanýsek, Irma C. Hernandez and Jianjiang Xu: Determination of choline, picrate, dodecylsulfate and several quaternary ammonium salts on an electrified liquid/liquid microinterfaces. Reprint from *Microchem. J.* **41**, 327–339 (1990). 22 June 1990.

ONR Technichal Report No. 029: Petr Vanýsek: Uncertainty in the potential of a reference interface in liquid/liquid measurements. Reprint from *Electroanalysis*, **2**, 409–413 (1990). 17 July 1990.

ONR Technichal Report No. 030: Jianjiang Xu: Electrochemical studies on gel/liquid interfaces. Master of Sciences defended thesis. 18 July 1990.

ONR Technichal Report No. 031: Petr Vanýsek and Irma C. Hernandez: Microscopic interface between two immiscible electrolytes: A parallelism to an ultramicroelectrode. Reprint from *Anal. Lett.* **23**, 771–785 (1990). 25 July 1990.

ONR Technichal Report No. 032: Petr Vanýsek: Electrochemical processes at liquid interfaces. Reprint from *Anal. Chem.* **62**, 827A–835A (1990). 29 August 1990.

ONR Technichal Report No. 033: Petr Vanýsek, Irma C. Hernandez and Jianjiang Xu: Supporting electrolytes for electrochemistry at liquid/liquid interfaces: Crystal violet and tetrabutylammonium tetraphenylborate in nitrobenzene. Galley proofs for an article in *J. Colloid Interface Sci.* 29 August 1990.

ONR Technichal Report No. 034: Richard P. Buck and Petr Vanýsek: Interfacial potential difference at mixed conductor interfaces: Nernst, Nernst–Donnan, Nernst distribution and generalizations. Galley proofs for an article in *J. Electroanal. Chem.* 29 August 1990.

ONR Technichal Report No. 035: Petr Vanýsek, Irma C. Hernandez and Jianjiang Xu: Supporting electrolytes for electrochemistry at liquid/liquid interfaces: Crystal violet and tetrabutylammonium tetraphenylborate in nitrobenzene. Reprint from *J. Colloid Interface Sci.* **139**, 527–534 (1990). 11 December 1990.

ONR Technichal Report No. 036: Interfacial potential difference at mixed conductor interfaces: Nernst, Nernst–Donnan, Nernst distribution and generalizations. Reprint from *J. Electroanal. Chem.* **292**, 73–91 (1990). 11 December 1990.

ONR Technichal Report No. 037: Multi-ion Nernst distribution potential equations: Interfacial potentials at equilibrium liquid/liquid and membrane interfaces. Reprint from *J. Electroanal. Chem.* **297**, 19–35 (1991). 3 April 1991.

ONR Technical Report No. 038: Antonín Tojánek and Petr Vanýsek: The resistance phenomena accompanying ion migration through a Nafion thin film membrane. Submitted manuscript to Journal of the Electrochemical Society. 12 April 1991.

ONR Technical Report No. 039: Petr Vanýsek and Jianjiang Xu: Gel solidified microinterface between two immiscible electrolytes applied to amperometric detection of picrate and tetramethylammonium. Progress report. 26 April 1991.

Published journal articles

Deborah H. Wiegand and Petr Vanýsek: Spectroscopic and fluorometric characterization of oxacyanine dyes in water and nitrobenzene. *Applied Spectroscopy*, **42**, 958 (1988).

Brenda D. Spangler, Petr Vanýsek, Irma C. Hernandez and Robin D. Rogers: Structure of crystal violet tetraphenylborate. *J. Cryst. Spec. Res.*, **19**, 589 (1989).

Petr Vanýsek: Impedance spectroscopy and impedance related problems in electrochemistry on the interface between two immiscible electrolytes. *Chimica Oggi*, **8** (January/February), 47–52 (1990).

Zhisheng Sun and Petr Vanýsek: Electrochemical determination of lead and lead ion transfer at liquid/liquid interfaces. *Anal. Chim. Acta*, **228**, 241–249 (1990)

Deborah H. Wiegand and Petr Vanýsek: Distribution of oxacyanine dyes between water and nitrobenzene: Determination of partition constants, association and potentials of transfer of dye cations on liquid/liquid interfaces. *J. Colloid Interface Sci.* **135**, 272–282 (1990).

P. Vanýsek: Uncertainty in potential of the reference interface in liquid/liquid measurements. *Electroanalysis* **2**, 409–413 (1990).

Petr Vanýsek and Zhisheng Sun: Bovine serum albumin adsorption on a water/nitrobenzene interface. *Bioelectrochem. Bioenerget.* **2**, 177–194 (1990).

Petr Vanýsek and Irma Hernandez: Microscopic interface between two immiscible electrolytes: A parallelism to an ultramicroelectrode. *Anal. Lett.* **23**, 771–785 (1990).

Petr Vanýsek, Irma C. Hernandez and Jianjiang Xu, Supporting electrolytes for electrochemistry on liquid/liquid interfaces: Crystal violet and tetrabutylammonium tetraphenylborate in nitrobenzene. *J. Colloid Interface Sci.* **139**, 527–534 (1990).

Petr Vanýsek and Irma C. Hernandez: Ion transport across a microscopic interface between two immiscible electrolytes, *J. Electrochem. Soc.*, **137**, 2763–2768 (1990).

Petr Vanýsek: Analytical applications of electrochemical processes on the interface between two immiscible electrolyte solutions, *Anal. Chem.*, **62**, 827A–835A (1990).

Petr Vanýsek, Irma C. Hernandez and Jianjiang Xu: Determination of choline, picrate, dodecylsulfate and several quaternary ammonium salts on an electrified liquid/liquid microinterface. *Microchem. J.*, **4**, 327–339 (1990).

Petr Vanýsek and Richard P. Buck: Multi-ion Nernst distribution potential equations: Interfacial potentials at equilibrium liquid/liquid and membrane interfaces. *J. Electroanal. Chem.*, 297, 19–35 (1991).

Richard P. Buck and Petr Vanýsek: Interfacial potential differences at non-classical interfaces: Nernst, Nernst–Donnan, Nernst distribution and generalizations. *J. Electroanal. Chem.*, 292, 73–91 (1990).

Submitted manuscripts

Petr Vanýsek: Interfacial ion transport in: M. Blank and I. Vodyanoy (Eds.), *Membrane Electrochemistry, Advances in Chemistry Series ACS*. Submitted.

Antonín Trojánek and Petr Vanýsek: The resistance phenomena accompanying ion migration through a Nafion thin film membrane. *J. Electrochem. Soc.*, Submitted (1991).

Personnel

Postdoctoral fellows

Zhisheng Sun (1988–1989)
Antonín Trojánek (1990–)

Graduate students

Deborah H. Wiegand (1987–1990)
Irma C. Hernandez (1988–1989)
Jianjiang Xu (1989–1990)
Alex Schreiner (1990–1991)
Giselle Sandi (1990–)

Undergraduate students

Judy Luebke (1987–1988)
Jan Huffaker (1988)
Amy Bove (1988)
Jennifer Schott (1988)
Tamy Rada (1988–1989)
Kirsten Fundanish (1988)
Marie A. Tovo (1989)
Peter Nickel (1990)
Alex Schreiner (1990)
Christina Staes (1990)
David Skotty (1990–)
Jennifer Keefer (1990)

Distribution list

Office of Naval Research
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, VA 22217-5000

Defense Technical Information Center
Building 5, Cameron Station
Alexandria, VA 22314

Resident Contract Administrator
Office of Naval Research
536 South Clark Street, Room 286
Chicago, IL 60605-1588