

## Editors

Prof. Dr. Gaston Berthier  
Université de Paris  
Institut de Biologie  
Physico-Chimique  
Fondation Edmond de Rothschild  
13, rue Pierre et Marie Curie  
F-75005 Paris

Prof. Dr. Michael J. S. Dewar  
Department of Chemistry  
The University of Texas  
Austin, Texas 78712/USA

Prof. Dr. Hanns Fischer  
Physikalisch-Chemisches Institut  
der Universität Zürich  
Rämistr. 76  
CH-8001 Zürich

Prof. Kenichi Fukui  
Kyoto University  
Dept. of Hydrocarbon Chemistry  
Kyoto/Japan

Prof. Dr. George G. Hall  
Department of Mathematics  
The University of Nottingham  
University Park  
Nottingham NG7 2RD/Great Britain

Prof. Dr. Jürgen Hinze  
Fakultät für Chemie  
Universität Bielefeld  
Postfach 8640  
D-4800 Bielefeld

Prof. Dr. Hans H. Jaffé  
Department of Chemistry  
University of Cincinnati  
Cincinnati, Ohio 45221/USA

Prof. Joshua Jortner  
Institute of Chemistry  
Tel-Aviv University  
61390 Ramat-Aviv  
Tel-Aviv/Israel

Prof. Dr. Werner Kutzelnigg  
Lehrstuhl für Theoretische Chemie  
der Universität Bochum  
Postfach 102148  
D-4630 Bochum 1

Prof. Dr. Klaus Ruedenberg  
Department of Chemistry  
Iowa State University  
Ames, Iowa 50010/USA

Prof. Jacopo Tomasi  
Dipartimento di Chimica e  
Chimica Industriale  
Università di Pisa  
Via Risorgimento, 35  
I-Pisa

# Lecture Notes in Chemistry

Edited by G. Berthier M. J. S. Dewar H. Fischer  
K. Fukui G. G. Hall J. Hinze H. H. Jaffé J. Jortner  
W. Kutzelnigg K. Ruedenberg J. Tomasi

39

---

P. Vanýsek

Electrochemistry on  
Liquid/Liquid Interfaces

---



Springer-Verlag  
Berlin Heidelberg New York Tokyo

**Author**

P. Vanýsek  
Northern Illinois University, Department of Chemistry  
DeKalb, IL 60115, USA

ISBN-13: 978-3-540-15677-2  
DOI: 10.1007/978-3-642-48910-5

e-ISBN-13: 978-3-642-48910-5

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically those of translation, reprinting, re-use of illustrations, broadcasting, reproduction by photocopying machine or similar means, and storage in data banks. Under § 54 of the German Copyright Law where copies are made for other than private use, a fee is payable to "Verwertungsgesellschaft Wort", Munich.

© by Springer-Verlag Berlin Heidelberg 1985

# Electrochemistry on Liquid/Liquid Interfaces

P. Vanýsek

Northern Illinois Univeristy, The Michael Faraday Laboratories  
Department of Chemistry, De Kalb, Illinois 60115, U.S.A.\*

## CONTENTS

I.	Introduction	3
II.	Theory	8
	Equilibrium Conditions	8
	The Nernst Potential	9
	Single Ion Gibbs Energy of Transfer	10
	Ideally Polarizable L/L Interface	21
	Redox System Equilibrium	22
III.	Experimental Arrangements	24
	Electrode Configuration	24
	Quasi-Reference Electrodes	25
	Reference Electrodes	25
	Four Electrode Potentiostat	26
	Convention of Signs	27
	Experimental Arrangements	27
	Electrolyte Dropping Electrode	28
	Stationary Interface	31
	Chronopotentiometry	33
	Cyclic Voltammetry	38
IV.	Double Layers at L/L Interfaces	40
V.	Current Flow Across the Interface	52
VI.	Mediated Properties	65
VII.	Impedance Measurements	79
	AC Bridges	85
	Lissajous Figures	86
	Phase Sensitive Detection	86
VIII.	Phase Transfer Catalysis	88
	References	90

---

\* The manuscript was prepared at the Chemistry Department of the University of New Hampshire, Durham, NH 03824. Author gratefully acknowledges support received from the department and extends his thanks for the use of a word processor and other facilities during the past year.

## List of symbols

a	activity
A	area
AC	alternating current
b	backward, bulk (in subscript)
Bu	butyl
c	concentration
C	capacitance
D	diffusion coefficient
DC	direct current
E	potential, energy
Et	ethyl
f	forward, frequency
F	Faraday constant
G	Gibbs energy of transfer
i	ion, current
I	current, imaginary (in subscript)
IR	voltage loss during current flow
ITIES	interface between two immiscible electrolyte solutions
j	current density, flux
k	rate constant
K	equilibrium constant
L	inductance
L/L	liquid/liquid
m	convolution integral
Me	methyl
n	nonaqueous, number of exchanged electrons
nb	nitrobenzene
o	oil (nonaqueous)
P	preexponential factor, phenyl
Pe	pentyl
Pr	propyl
PTC	phase transfer catalysis
PZC	potential of zero charge
r	radius
R	resistance, real (in subscript), gas constant
t	time
tr	transfer
T	absolute temperature
TBA	tetrabutylammonium
TEA	tetraethylammonium
TMA	(also TMeA) tetramethylammonium
TPAs	tetraphenylarsonium
TPB	tetraphenylborate
U	potential
V	potential
w	water, aqueous phase
z	charge on transporting ion
Z	impedance
$\alpha$	charge transfer coefficient
$\beta$	$1 - \alpha$
$\Delta$	difference
$\epsilon$	permittivity
$\mu$	chemical potential
$\mu$	electrochemical potential
$\tau$	transition time, time constant
$\phi$	Galvani (inner) potential, electrostatic potential, phase angle
$\omega$	circular frequency