

Contents

Introduction

| | |
|---------------------------|---|
| V. E. Kazarinov | 1 |
|---------------------------|---|

Electrolysis at the Interface Between Two Immiscible Electrolyte Solutions

| | |
|------------------------------------|---|
| J. Koryta | 3 |
| Theory | 3 |
| Experimental Procedures | 8 |
| Results and Applications | 9 |
| References | 9 |

Problems of a Quantum Theory of Charge Transfer Reactions at the Interface Between Two Immiscible Liquids

| | |
|---|----|
| A. M. Kuznetsov, Yu. I. Kharkats | 11 |
| 1. The Franck-Condon Principle and the Physical Mechanism of the Transition | 11 |
| 2. The Role of a Polar Medium and the Solvent Model | 14 |
| 3. The Reorganization Energy of the Medium | 17 |
| 4. The Role of Intramolecular Vibrations and Quantum Degrees of Freedom | 22 |
| 5. General Regularities in Charge Transfer Processes at the Interface Between Immiscible Liquids | 23 |
| 6. Electron Transfer at the Interface of Two Immiscible Liquids | 26 |
| 7. Ion Transfer Through the Interface | 34 |
| 8. Conclusion | 45 |
| References | 45 |

Hydrodynamics and Mass Exchange at the Phase Boundaries with Regular Dissipative Structures

| | |
|--|----|
| V. S. Krylov | 47 |
| 1. Introduction | 47 |
| 2. General Theoretical Description of Dissipative Structures | 47 |

| | |
|---|----|
| 3. Capillary Instability Due to the Marangoni Effect | 51 |
| 4. Electro-hydrodynamic Instability | 53 |
| 5. The Linear Analysis of Marangoni Instability | 54 |
| 6. The Instability Caused by the Electric Forces Acting at the Surface of an Electrolyte Solution | 59 |
| 7. Nonlinear Methods of Analyzing the Marangoni Instability | 63 |
| 8. Models of Systems with Regular Hydrodynamic Dissipative Structures | 64 |
| 9. Regular Circulation Fluxes Caused by Hydrodynamic Instability and their Role in Interfacial Mass Exchange | 71 |
| 10. Conclusion | 73 |
| References | 74 |

Galvani and Volta Potentials at the Interface Separating Immiscible Electrolyte Solutions

| | |
|---|-----|
| Z. Koczorowski | 77 |
| Abstract | 77 |
| 1. Introduction | 77 |
| 2. Liquid Galvanic Cells – a Historical Survey | 79 |
| 2.1 Investigations of the Nernst Type Cells | 80 |
| 2.2 Investigations of the Haber Type Cells | 81 |
| 2.3 Other Types of Liquid Cells | 83 |
| 3. Galvani Potential at the Interface of Immiscible Electrolyte Solutions | 83 |
| 3.1 General Approach of Le Hung | 84 |
| 3.2 Distribution Potentials for Binary Electrolytes | 85 |
| 3.3 Interfaces Reversible with Respect to Single Ions | 88 |
| 3.4 Experimental Investigations of Galvani Potentials of Nonpolarizable Interfaces | 89 |
| 3.5 Ion Transfer Energies and Galvani Potentials | 93 |
| 4. Polarizable Interface of Immiscible Electrolyte Solutions | 97 |
| 5. Volta Potentials at the Interfaces of Immiscible Electrolyte Solutions | 99 |
| 6. Final Observations | 102 |
| References | 102 |

Electrocapillarity and the Electric Double Layer Structure at Oil/Water Interfaces

| | |
|---|-----|
| M. Senda, T. Kakiuchi, T. Osakai, T. Kakutani | 107 |
| Summary | 107 |
| Ideal-Polarized and Nonpolarized Oil/Water Interfaces | 109 |
| Electrocapillary Curves of Ideal-Polarized Oil/Water Interfaces | 111 |
| Electrocapillary Curves of Nonpolarized Oil/Water Interfaces | 118 |
| References | 120 |

Study of the Electrical Double Layer at the Interface Between Two Immiscible Electrolyte Solutions by Impedance Measurements

| | |
|--|-----|
| Z. Samec, V. Mareček | 123 |
| Thermodynamic Background | 123 |
| AC Impedance Measurements | 125 |
| Galvanostatic Pulse Technique | 129 |
| Capacitance Data | 133 |
| Zero-Charge Potential Difference | 135 |
| Inner-Layer Potential Difference and Capacitance | 136 |
| References | 140 |

Redox and Photochemical Reactions at the Interface Between Immiscible Liquids

| | |
|---|-----|
| L. I. Boguslavsky, A. G. Volkov | 143 |
| I. Introduction | 143 |
| II. Redox Reactions in Monolayers | 144 |
| III. Redox Processes in the Oil/Water System when Donor and Acceptor are Contained in Different Phases | 145 |
| 1. Evidence for the Occurrence of the Process | 145 |
| 2. Influence of Specific Adsorption of Halogen Ions on the Reduction of Hydrophobic Porphyrin | 145 |
| IV. Metalcomplexes of Porphyrins – Catalysts of Redox Reactions at the Interface Between Immiscible Liquids | 148 |
| 1. Redox Reactions Involving Chlorophyll | 148 |
| 2. Adsorption of Chlorophyll at the Oil/Water Interface | 148 |
| 3. Redox Reactions Catalyzed by Chlorophyll in the Oil/Water System | 149 |
| 4. Formation of the Boundary Layer Enriched in Protons | 150 |
| 5. Redox Reactions Catalyzed by Other Metalloporphyrins | 151 |
| V. Evidence for the Heterogeneity of Redox Reactions Catalyzed by Metalcomplexes of Porphyrins | 152 |
| 1. Adsorption of Catalyst at the Interface | 153 |
| 2. Cause of the Potential Shift and its Proportionality to the Concentration of Adsorbed Catalyst | 154 |
| VI. Enzyme Complexes of the Mitochondrial Respiratory Chain in the Oil/Water Interface | 156 |
| VII. Redox Reactions in the Oil/Water System Accompanied by Protonation of Acceptor in the Nonaqueous Phase | 160 |
| 1. Enzyme-Catalyzed Redox Reactions Accompanied by Capture of Proton by Acceptor in the Nonaqueous Phase | 160 |
| 2. Chlorophyll-Catalyzed Redox Reaction Accompanied by the Capture of Proton Acceptor in the Nonaqueous Phase | 163 |
| 3. Photooxidation of Water Catalyzed by Chlorophyll Adsorbed at the Interface Between Two Immiscible Liquids | 164 |

| | |
|--|-----|
| 4. Carotene – a Photosensitizer of the Water Photooxidation Reaction | 167 |
| 5. Possible Mechanism of Water Photooxidation Sensitized by Chlorophyll | 170 |
| 6. Reaction Thermodynamics | 170 |
| VIII. Coupling of Reactions at the Interface Between Immiscible Liquids . . . | 173 |
| References | 176 |

Counterions and Adsorption of Ion-Exchange Extractants at the Water/Oil Interface

| | |
|---|-----|
| A. N. Popov | 179 |
| Abstract | 179 |
| The Water/Oil Interface and Extraction Processes | 180 |
| Adsorption and Extraction Constants | 181 |
| Counterions and Adsorption of Extractants | 184 |
| 1. Alkylammonium Salts | 184 |
| 2. Cation-Exchange Extractants | 194 |
| 3. Macrocyclic Ionophores | 195 |
| Determination of Activity Coefficients for Extractants in Low-Permittivity Media from Surface Pressure Isotherms | 199 |
| References | 202 |

Kinetics of the Photochemical Charge Separation in Micellar Solutions

| | |
|---|-----|
| M. G. Kuzmin, N. K. Zaitsev | 207 |
| 1. The Formal Kinetics of Reactions in Micellar Systems | 207 |
| 1.1 Solubilization of Molecules by Surfactant Micelles and the Distribution of Reactant Molecules Among Micelles | 207 |
| 1.1.1 The Pseudophase and Microscopic Models of Solubilization | 207 |
| 1.1.2 Solubilization as a Kind of Interphase Equilibrium | 208 |
| 1.1.3 The Effect of the Intermicellar Distribution of Reactant Molecules | 211 |
| 1.2 The Interfacial Exchange of Molecules in Microheterogeneous Solutions | 212 |
| 1.2.1 The Exchange of Molecules at the Interface Between Micelles and Bulk Phase | 212 |
| 1.2.2 First-Order Reaction in Micellar Solutions | 213 |
| 1.2.3 Second-Order Photoreactions in Micellar Solutions. CMC Measurements and Aggregation Numbers | 214 |
| 1.2.4 Reversible Reactions | 219 |
| 2. Charge Separation in Micellar Systems | 221 |
| 2.1 Micelles as Media for Photochemical Reactions | 221 |
| 2.1.1 Models of Micellar Solutions Influencing the Reactivity of the Solubilizates | 221 |
| 2.1.2 The Effective Microviscosity and Polarity of Micelles | 221 |

| | |
|--|------------|
| 2.2 Initial Charge Separation and Geminate Recombination in Micellar Systems | 224 |
| 2.2.1 Photoionization in Micellar Solutions | 224 |
| 2.2.2 Photoprotolytic Dissociation in Micellar Solutions | 226 |
| 2.2.3 Second-Order Intramicellar Electron Transfer Reactions | 229 |
| 2.2.4 Bimolecular Proton Transfer Reactions | 232 |
| 2.3 Initial Stabilization of the Charge Separation Products | 233 |
| 2.4 Bulk Recombination of Separated Charges and Mass Exchange at the Interface | 234 |
| 2.4.1 Effect of the Micellar Potential upon the Bulk Recombination of Charge Carriers | 234 |
| 2.4.2 Effect of the Hydrophobic Balance of Reactants upon their Solubilization | 236 |
| 2.4.3 Molecule Exchange at the Interface | 237 |
| 2.5 Stabilization of the Separated Charges in Systems with Mediators | 238 |
| 3. Conclusion | 239 |
| References | 241 |
| | |
| Subject Index | 245 |