

Contents

Preface to the First Edition *XI*
Preface to the Second Edition *XIII*

Part One Fundamentals of Chemistry in Nonaqueous Solutions: Electrochemical Aspects 1

- 1 Properties of Solvents and Solvent Classification 3**
 - 1.1 Properties of Solvents 8
 - 1.1.1 Physical Properties of Solvents 8
 - 1.1.2 Chemical Properties of Solvents 13
 - 1.1.3 Structural Aspects of Solvents 17
 - 1.1.4 Toxicity and Hazardous Properties of Solvents 19
 - 1.2 Classification of Solvents 20
 - 1.3 Effects of Solvent Properties on Chemical Reactions:
An Outline 22
References 24

- 2 Solvation and Complex Formation of Ions and Behavior
of Electrolytes 27**
 - 2.1 Influence of Ion Solvation on Electrolyte Dissolution 27
 - 2.2 Some Fundamental Aspects of Ion Solvation 29
 - 2.2.1 Ion–Solvent Interactions Affecting Ion Solvation 29
 - 2.2.2 Structure of Solvated Ions 36
 - 2.2.3 Ultrafast Ion Solvation Dynamics 39
 - 2.3 Comparison of Ionic Solvation Energies in Different Solvents and
Solvent Effects on Ionic Reactions and Equilibria 40
 - 2.3.1 Gibbs Energies of Transfer and Transfer Activity Coefficients
of Ions 40
 - 2.3.2 Prediction of Solvent Effects by the Use of Transfer Activity
Coefficients 44
 - 2.4 Solvent Effects on the Complexation of Metal Ions 46

2.5	Selective Solvation of Ions in Mixed Solvents	49
2.6	Ion Association and Solvent Permittivities	53
	References	59
3	Acid–Base Reactions in Nonaqueous Solvents	63
3.1	Solvent Effects on Acid–base Reactions	63
3.1.1	Acid–Base Reactions in Amphiprotic Solvents of High Permittivity	64
3.1.2	Acid–Base Reactions in Aprotic Solvents of High Permittivity	69
3.1.3	Acid–Base Reactions in Amphiprotic Solvents of Low Permittivity	79
3.1.4	Acid–Base Reactions in Aprotic Solvents of Low Permittivity	79
3.2	pH Scales in Nonaqueous Solutions	80
3.2.1	Definition of pH in Nonaqueous Solutions	80
3.2.2	pH Windows in Nonaqueous Solvents and pH Scales Common to Multisolvents	82
	References	86
4	Redox Reactions in Nonaqueous Solvents	89
4.1	Solvent Effects on Various Types of Redox Reactions	89
4.1.1	Fundamentals of Redox Reactions	89
4.1.2	Solvent Effects on Redox Potentials and Redox Reaction Mechanisms	93
4.1.3	Dynamical Solvent Effects on the Kinetics of Redox Reactions	100
4.2	Redox Properties of Solvents and Potential Windows	103
4.3	Redox Titrations in Nonaqueous Solutions	106
4.3.1	Titration with Oxidizing Agents	106
4.3.2	Titration with Reducing Agents	109
	References	110
Part Two	Electrochemical Techniques and Their Applications in Nonaqueous Solutions	111
5	Overview of Electrochemical Techniques	113
5.1	Classification of Electrochemical Techniques	113
5.2	Fundamentals of Electrode Reactions and Current–Potential Relations	114
5.2.1	Current–Potential Relation for Electron Transfer at the Electrode	115
5.2.2	Current–Potential Relations and Mass Transport	118
5.3	DC Polarography – Methods that Electrolyze Electroactive Species Only Partially (1)	121
5.4	New Types of Polarography – Methods that Electrolyze Electroactive Species Only Partially (2)	129
5.4.1	AC Polarography	130
5.4.2	SW Polarography	131
5.4.3	Pulse Polarography	131

5.5	Voltammetry and Related New Techniques – Methods that Electrolyze Electroactive Species Only Partially (3)	133
5.5.1	Linear Sweep Voltammetry	134
5.5.2	Cyclic Voltammetry	136
5.5.3	Voltammetry at Rotating Disk and Rotating Ring-Disk Electrodes	138
5.5.4	Ultramicroelectrodes	140
5.5.5	Modified Electrodes	141
5.5.6	Other Items Related to Voltammetry	142
5.5.7	Combination of Voltammetry and Nonelectrochemical Methods	144
5.6	Electrogravimetry and Coulometry – Methods that Completely Electrolyze Electroactive Species	147
5.6.1	Controlled-Potential Electrolysis and Controlled-Current Electrolysis	147
5.6.2	Electrogravimetry	149
5.6.3	Coulometry and Coulometric Titrations	150
5.7	Potentiometry – A Method that Does Not Electrolyze Electroactive Species	152
5.7.1	Potentiometric Indicator Electrodes and Reference Electrodes	153
5.7.2	Potentiometric Titrations	157
5.8	Conductimetry – A Method that Is Not Based on Electrode Reactions	158
5.9	Electrochemical Instrumentation – Roles of Operational Amplifiers and Microcomputers	161
5.9.1	Application of Operational Amplifiers in Electrochemical Instrumentation	161
5.9.2	Application of Personal Computers in Electrochemical Instrumentation	167
	References	167
6	Potentiometry in Nonaqueous Solutions	171
6.1	Basic Techniques of Potentiometry in Nonaqueous Solutions	171
6.1.1	Potentiometric Indicator Electrodes for Nonaqueous Solutions	172
6.1.2	Reference Electrodes for Nonaqueous Solutions	172
6.1.3	Method of Reporting Electrode Potentials in Nonaqueous Solutions (IUPAC Recommendation)	175
6.1.4	Liquid Junction Potential Between Electrolyte Solutions in the Same Solvent	178
6.2	pH Measurements in Nonaqueous and Mixed Solvents	180
6.2.1	IUPAC Method of pH Measurements in Aqueous Solutions	180
6.2.2	Methods of pH Measurements in Nonaqueous and Mixed Solvents	182
6.2.3	Determination of Autoprotolysis Constants	186
6.3	Applications of Potentiometry in Nonaqueous Solutions	188
6.3.1	Acid–Base Reactions in Nonaqueous Solvents	188

6.3.2	Precipitation Reactions in Nonaqueous Solutions	192
6.3.3	Complex Formation Reactions in Nonaqueous Solutions	192
6.3.4	Redox Reactions in Nonaqueous Solutions	194
6.3.5	Potentiometric Characterization of Solvents	196
6.3.6	Potentiometric Study of Ion Solvation – Applications that Compare Electrode Potentials in Different Solvents	196
6.4	Liquid Junction Potentials between Different Solvents	201
	References	206
7	Conductimetry in Nonaqueous Solutions	209
7.1	Dissociation of Electrolytes and Electrolytic Conductivity	209
7.1.1	Molar Conductivity of Dilute Solutions of Symmetrical Strong Electrolytes	209
7.1.2	Molar Conductivity and Association Constants of Symmetrical Weak Electrolytes	210
7.1.3	Molar Conductivity and the Formation of Triple Ions	213
7.1.4	Conductivity of Solutions of Symmetrical Strong Electrolytes at Moderate to High Concentrations	214
7.1.5	Molar Conductivity and Ion Association of Asymmetric Electrolytes	216
7.2	Ionic Conductivities and Solvents	217
7.2.1	Stokes' Law and Walden's Rule – Role of Ultrafast Solvent Dynamics	217
7.2.2	Method for the Determination of Limiting Molar Conductivities of Ions	221
7.3	Applications of Conductimetry in Nonaqueous Solutions	222
7.3.1	Study of the Behavior of Electrolytes (Ionophores)	222
7.3.2	Conductimetric Studies of Acid–Base Equilibria	227
	References	230
8	Polarography and Voltammetry in Nonaqueous Solutions	233
8.1	Basic Experimental Techniques in Nonaqueous Solutions	233
8.1.1	Experimental Apparatus for Nonaqueous Systems	233
8.1.2	Solvents and Supporting Electrolytes	236
8.2	Polarography and Voltammetry of Inorganic Species	237
8.2.1	Polarographic Reductions of Metal Ions	237
8.2.2	Polarography and Voltammetry of Metal Complexes	247
8.2.3	Polarography and Voltammetry of Anions	251
8.2.4	Electrode Reactions of Dissolved Oxygen, Dissolved Hydrogen, Carbon Dioxide and Solvated Electrons	253
8.3	Polarography and Voltammetry of Organic Compounds	255
8.3.1	Reductions of Organic Compounds	255
8.3.2	Oxidation of Organic Compounds	268
8.4	Cyclic Voltammetry for Electrochemical Studies in Nonaqueous Solutions	274

8.4.1	Digital Simulation in Cyclic Voltammetry	274
8.4.2	Ultramicroelectrodes in Cyclic Voltammetry	275
8.4.3	Low-Temperature Electrochemistry and Cyclic Voltammetry	277
8.5	Voltammetry of Isolated Nanoparticle Solutions (Nanoelectrochemistry)	278
	References	281
9	Other Electrochemical Techniques in Nonaqueous Solutions	287
9.1	Use of Electrolytic and Coulometric Techniques in Nonaqueous Solutions	287
9.2	Combination of Electrochemical and Nonelectrochemical Techniques	289
9.2.1	Spectroelectrochemistry	289
9.2.2	Electrochemical-ESR Method	296
9.2.3	Electrochemical Mass Spectroscopy	299
9.2.4	Use of Electrochemical Quartz Crystal Microbalance	301
9.2.5	Use of Scanning Electrochemical Microscopy	301
	References	304
10	Purification of Solvents and Tests for Impurities	307
10.1	Effects of Solvent Impurities on Electrochemical Measurements	308
10.2	Procedures for the Purification of Solvents	309
10.3	Tests for Purity of Solvents	311
10.4	Purification Methods for Solvents in Common Use	314
	References	320
11	Selection and Preparation of Supporting Electrolytes	321
11.1	Selection of Supporting Electrolytes for Electrochemical Measurements	321
11.1.1	Solubility and Conductivity of Supporting Electrolytes	321
11.1.2	Potential Windows and Supporting Electrolytes	324
11.1.3	Influences of Supporting Electrolytes on Electrode Reactions in Nonaqueous Solutions	326
11.2	Methods for Preparing and Purifying Supporting Electrolytes	328
	References	330
12	Use of Nonaqueous Solutions in Modern Electrochemical Technologies	333
12.1	Batteries Using Nonaqueous Solutions – Lithium Batteries	333
12.2	Capacitors Using Nonaqueous Solutions	337
12.2.1	Electrochemical Double-Layer Capacitors and Pseudocapacitors	337
12.2.2	Aluminum Electrolytic Capacitors	339
12.3	Conducting Polymers and Electrochemistry in Nonaqueous Solutions	340
12.4	Electrochemiluminescence (ECL)	343

12.5	Electrochemical Reduction of CO ₂ in Nonaqueous Solutions	346
12.6	Use of Acetonitrile in Electrowinning and Electrorefining of Copper	349
12.7	Electrodeposition of Metals and Semiconductors from Nonaqueous Solutions	351
	References	352

Part Three Electrochemistry in New Solvent Systems 355

13	Electrochemistry in Clean Solvents	357
13.1	Introduction	357
13.2	Supercritical Fluids	358
13.2.1	General Aspects of Supercritical Fluids	358
13.2.2	Electrochemical Aspects of Supercritical Fluids	362
13.3	Ionic Liquids	364
13.3.1	Physical, Chemical and Electrochemical Properties of ILs	366
13.3.2	Voltammetry in ILs	372
13.3.3	Applications of ILs in Electrochemical Technologies	376
13.3.4	Risks of ILs and Their Decomposition	379
	References	381
14	Electrochemistry at the Liquid–Liquid Interfaces	385
14.1	Interfaces Between Two Immiscible Electrolyte Solutions (ITIES)	385
14.1.1	Fundamentals of Electrochemistry at the ITIES	385
14.1.2	Practical Applications of Electrochemistry at the ITIES	392
14.1.3	Three-Phase Electrochemistry	394
14.2	Interfaces Between Ionic Liquids and Water	395
14.2.1	Fundamentals	395
14.2.2	Salt Bridges and Reference Electrodes	397
14.2.3	Potential Windows and Voltammograms	397
	References	399

Index	401
--------------	------------