

## Contents

<b>1</b>	<b>An Introduction to Ionic Liquids</b>	<b>1</b>
1.1	Prologue	1
1.2	The Definition of an Ionic Liquid	2
1.3	A Brief Perspective	6
1.4	Aprotic Versus Protic ILs	8
1.5	An Overview of IL Applications	9
1.6	Key Properties and Techniques for Understanding ILs	12
1.6.1	Viscosity	12
1.6.2	Vapor Pressure	13
1.6.3	Melting Point	13
1.6.4	Nanostructure	14
1.6.5	Thermal Properties	14
1.6.6	Electrochemical Properties	16
1.6.7	Conductivity and Ion Transport	16
1.6.8	Computational Techniques	17
1.7	New Materials Based on ILs	18
1.8	Nomenclature and Abbreviations	20
	References	20
<b>2</b>	<b>The Structure of Ions that Form Ionic Liquids</b>	<b>27</b>
2.1	Introduction	27
2.2	Ionic Interactions and the Melting Point	28
2.2.1	Thermodynamics of the Melting Point	29
2.3	Effect of Ion Size and Crystal Packing	31
2.3.1	Quantifying the Madelung Constant	34
2.3.2	Computational Prediction of the Melting Point	35
2.4	Charge Delocalization and Shielding	37
2.5	Ion Asymmetry	39
2.6	Influence of Cation Substituents	41
2.7	Degrees of Freedom and Structural Disorder	43
2.7.1	Polymorphism	44
2.8	Short-Range Interactions – Hydrogen Bonding	44

2.9	Dications and Dianions	47
2.10	$T_m$ Trends in Other IL Families	49
2.11	Concluding Remarks	50
	References	50
<b>3</b>	<b>Structuring of Ionic Liquids</b>	55
3.1	Introduction	55
3.2	Ionicity, Ion Pairing and Ion Association	56
3.3	Short-Range Structuring	58
3.4	Structural Heterogeneity and Domain Formation	60
3.5	Hydrogen Bonding and Structure	62
3.6	Experimental Probes of Structure	64
3.7	Simulation Approaches to Understanding Structure	67
3.8	Structuring at Solid Interfaces	71
3.9	Ionic Liquid Structure in Confined Spaces	74
3.10	Impact of Structure on Reactivity and Application	75
3.11	Concluding Remarks	76
	References	76
<b>4</b>	<b>Synthesis of Ionic Liquids</b>	81
4.1	Introduction	81
4.2	Synthesis of ILs	81
4.2.1	Formation of the Cation: Quaternization/Alkylation	81
4.2.2	Anion Exchange	82
4.2.2.1	Metathesis	83
4.2.2.2	Purification and Challenges of the Metathesis Reaction	84
4.2.2.3	Ion Exchange	85
4.2.3	Synthesis of ILs via the Carbonate Route	86
4.2.4	Flow Reactors	87
4.2.5	Solvate ILs	89
4.2.6	Chloroaluminate ILs	90
4.2.7	Task-Specific Ionic liquids (TSILs)	90
4.2.7.1	Alkoxy-Ammonium ILs	90
4.2.7.2	Zwitterionic Liquids	91
4.2.8	One-Pot Synthesis of Multi-Ion ILs	92
4.2.9	Polymer Ionic Liquids (Poly-ILs)	93
4.2.10	Protic Ionic Liquids (PILs)	95
4.2.11	Chiral ILs	96
4.3	Characterization and Analysis of ILs	97
4.4	Concluding Remarks	98
	References	99
<b>5</b>	<b>Physical and Thermal Properties</b>	103
5.1	Introduction	103
5.2	Phase Transitions and Thermal Properties	103
5.2.1	Thermal Analysis and the Key Transitions Defining the Liquid State	103

5.2.2	Glass Transition, Glassy ILs, and the Kauzman Paradox	104
5.2.3	The Ideal Glass Transition	107
5.2.4	Influence of Ion Structure on $T_g$	108
5.2.5	Solid–Solid Transitions	109
5.2.5.1	Plastic Crystalline Phases	109
5.2.5.2	Liquid Crystals	110
5.2.6	Vaporization	110
5.2.7	Thermal Decomposition	113
5.2.8	Thermal Conductivity and Heat Capacity	117
5.3	Surface and Tribological Properties	118
5.4	Transport Properties and their Inter-relationships	120
5.4.1	Temperature Dependence of Transport Properties	124
5.4.2	Ionicity and the Walden Plot	126
5.4.2.1	Modeling the Transport Properties of ILs.	128
5.5	Properties of Ionic Liquid Mixtures	129
5.5.1	Thermal Properties	130
5.5.1.1	Melting Behavior of Mixtures of Salts and the Entropy of Mixing	130
5.5.1.2	Eutectics	132
5.5.2	Excess Molar Volume ( $V^E$ )	134
5.5.3	Viscosity	135
5.5.4	Conductivity	136
5.5.5	Ionicity	137
5.6	Protic ILs, Proton Transfer, and Mixtures	139
5.7	Deep Eutectic Solvents and Solvate ILs	141
5.8	Concluding Remarks	142
	References	143
<b>6</b>	<b>Solvent Properties of Ionic Liquids: Applications in Synthesis and Separations</b>	<b>149</b>
6.1	Introduction – Solvency and Intermolecular Forces	149
6.2	Liquid–Liquid Phase Equilibrium	151
6.2.1	Liquid Solubility, Mixing, and Demixing	151
6.2.2	Solvent Extraction	152
6.3	Gas Solubility and Applications	154
6.3.1	Physical Dissolution of Gases	154
6.3.2	Chemical Dissolution of Gases	158
6.4	Synthetic Chemistry in ILs – Selected Examples	159
6.4.1	Solvent Control of Reactions – Toluene + $\text{HNO}_3$	160
6.4.2	Recovery of Expensive Catalysts: The Heck Reaction	161
6.4.3	Increased Reaction Rates and Enantiomeric Selectivity in Diels–Alder Reactions	162
6.4.4	Modulation of the Lewis Acidity of Catalysts: The Friedel–Crafts Reaction	163
6.4.5	Shift in Equilibrium by Stabilizing the Intermediate Species in the Rate-Determining Step: the Baylis–Hilman Reaction	165
6.4.6	Increase in Rate Constant at Low IL Concentrations: Substitution Reactions	166

6.5	Inorganic Materials Synthesis	167
6.6	Biomass Dissolution	169
6.6.1	Cellulose and Lignocellulose	169
6.6.2	Chitin	170
6.6.3	Keratin	170
6.6.4	Wool	171
6.6.5	Silk	171
6.7	Concluding Remarks	172
	References	172
<b>7</b>	<b>Electrochemistry of and in Ionic Liquids</b>	<b>177</b>
7.1	Basic Principles of Electrochemistry in Nonaqueous Media	177
7.1.1	Redox Potentials	177
7.1.2	Three-Electrode Measurements	178
7.1.3	Potential Scanning Techniques	179
7.1.4	Reference Electrodes in IL Media	180
7.2	The Electrochemical Window of Ionic Liquids	182
7.2.1	The Effect of Impurities	183
7.2.2	Choice of Working Electrode	184
7.2.3	Other Factors Affecting the Electrochemical Window	184
7.3	Redox Processes in ILs	185
7.3.1	Internal Calibrants	185
7.3.2	Redox Couples for DSSCs	185
7.3.3	Metal Bipyridyl Complexes	187
7.3.4	Organic Redox Reactions	188
7.3.5	Polyoxometallates	189
7.3.6	Redox-Active ILs	190
7.4	Electrodeposition and Cycling of Metals in ILs	191
7.4.1	Chloroaluminate-Based ILs	193
7.4.2	Zinc	193
7.4.3	Aluminium Deposition from Air and Water Stable ILs	193
7.4.4	Lithium	194
7.4.5	Sodium	194
7.4.6	Magnesium	194
7.5	Electrosynthesis in Ionic Liquids	195
7.5.1	Oxidation Reactions	197
7.5.1.1	Fluorination	197
7.5.1.2	Oxidation of Alcohols	198
7.5.2	Reduction Reactions	199
7.5.2.1	CO <sub>2</sub> Reduction	199
7.5.2.2	Carbon–Carbon Bond Formation	200
7.6	Concluding Remarks	202
	References	202
<b>8</b>	<b>Electrochemical Device Applications</b>	<b>209</b>
8.1	Introduction	209
8.2	Batteries	210

8.2.1	Lithium–Ion Battery	210
8.2.2	High-Voltage Cathodes	214
8.2.3	Alternative High-Energy-Density Batteries	215
8.3	Fuel Cells	216
8.4	Dye-Sensitized Solar Cells and Thermoelectrochemical Cells	220
8.5	Supercapacitors	223
8.6	Actuators	225
8.7	Concluding Remarks	226
	References	227
<b>9</b>	<b>Biocompatibility and Biotechnology Applications of Ionic Liquids</b>	<b>231</b>
9.1	Biocompatibility of Ionic Liquids	231
9.1.1	Chemical Toxicity	231
9.1.2	Osmotic Toxicity	232
9.1.3	Biodegradation	233
9.1.4	Hydrated Ionic Liquids	234
9.2	Ionic Liquids from Active Pharmaceutical Ingredients	234
9.2.1	Dual Actives	235
9.2.2	Patent Matters	236
9.2.3	Protic Forms of APIs	236
9.2.4	Antimicrobials	237
9.2.5	Other Actives – Pesticides and Herbicides	237
9.3	Biomolecule Stabilization in IL Media	238
9.3.1	Proteins	238
9.3.2	DNA and RNA	239
9.3.3	Buffer ILs	241
9.3.4	Structural Proteins	242
9.4	Concluding Remarks	242
	References	243

**Index** 245

