

# Contents

<b>Chapter 1</b>	<b>Introduction</b>	<b>1</b>
	1.1 Definition of Ionic Liquids	1
	1.2 Synonyms	1
	1.3 Attraction of Ionic Liquids	2
	1.4 Cations and Anions	3
	1.5 Shorthand Notation for Cations and Anions	4
	1.6 Aprotic and Protic Ionic Liquids	5
	1.7 Binary Mixtures	6
	1.8 Organic and Inorganic Ionic Liquids	6
	1.9 Deep Eutectic Solvents	6
	1.10 Task-specific Ionic Liquids	7
	1.11 Chiral Ionic Liquids	8
	1.12 Generations of Ionic Liquids	8
	References	10
<b>Chapter 2</b>	<b>History</b>	<b>12</b>
	2.1 Origins	12
	2.2 Key Dates in the History of Ionic Liquids	13
	References	16
<b>Chapter 3</b>	<b>Synthesis of Ionic Liquids</b>	<b>19</b>
	3.1 Introduction	19
	3.2 Alkylation	20
	3.3 Anion Exchange	20
	3.4 Microwave- and Ultrasound-assisted Synthesis	23
	3.5 Halide-free Synthesis	23

---

An Introduction to Ionic Liquids

By Michael Freemantle

© Michael Freemantle 2010

Published by the Royal Society of Chemistry, [www.rsc.org](http://www.rsc.org)

3.6	Synthesis by Protonation	24
3.7	Synthesis of Haloaluminate Ionic Liquids	25
3.8	Synthesis of Task-specific Ionic Liquids	25
3.9	Chiral Synthesis	27
	References	29
<b>Chapter 4</b>	<b>Properties of Ionic Liquids</b>	<b>31</b>
4.1	Introduction	31
4.2	Liquid Range and Thermal Stability	32
4.3	Melting Points	32
4.4	Vapour Pressure	33
4.5	Heat Capacity and Heat Transfer	34
4.6	Viscosity	34
4.7	Density	35
4.8	Solubility and Miscibility	35
4.9	Water Stability	35
4.10	Conductivity	36
4.11	Electrochemical Potential Window	36
4.12	Surface Tension	36
4.13	Fluorescence	37
4.14	Refractive Indices	37
4.15	Impact of Impurities	38
	References	39
<b>Chapter 5</b>	<b>Ionic Liquids as Designer Solvents</b>	<b>41</b>
5.1	Introduction	41
5.2	Solubility and Miscibility	42
5.3	Polarity and Solvation	43
5.4	Miscibility with Water	44
5.5	Miscibility with Organic Compounds	44
5.6	Solubility of Metal Salts	46
5.7	Gas Solubility	46
5.8	Biphasic Systems	48
5.9	Phase Diagrams	48
5.10	Partitioning of Solutes between Ionic Liquids and Water	52
5.11	Biphasic Systems of Hydrophilic Ionic Liquids and Water	53
5.12	Mutually Immiscible Ionic Liquids	53
5.13	Separations and Extractions	54
5.14	Extraction of Organic Compounds	54
5.15	Gas Separations	56
5.16	Carbon Dioxide Extractions and Separations	57

5.17	Metal Ion Extractions	58
5.18	Extractive Distillations	60
5.19	Membrane Separations	61
	References	62
<b>Chapter 6</b>	<b>Green Credentials of Ionic Liquids</b>	<b>65</b>
6.1	Introduction	65
6.2	Vapour Pressure	68
6.3	Flammability and Combustibility	70
6.4	Recycling	71
6.5	Environmental Exposure and Toxicity	72
6.5.1	Release into the Environment	72
6.5.2	Spatiotemporal Range	73
6.5.3	Biodegradability	73
6.5.4	Biological Activity	73
6.5.5	Bioaccumulation	75
	References	77
<b>Chapter 7</b>	<b>Electrochemistry</b>	<b>79</b>
7.1	Introduction	79
7.2	Cyclic Voltammetry	80
7.3	Batteries	83
7.4	Fuel Cells	85
7.5	Dye-sensitized Solar Cells	86
7.6	Electrodeposition	88
7.7	Actuators	91
7.8	Supercapacitors	92
7.9	Electrosynthesis	94
	References	95
<b>Chapter 8</b>	<b>Catalysis</b>	<b>99</b>
8.1	Introduction	99
8.2	Monophasic and Biphasic Catalysis	100
8.3	Solvents, Catalysts and Ligands	101
8.4	Catalyst Performance	105
8.5	Supported Ionic Liquid Catalysis	108
8.6	Nanoparticle Catalysts	110
8.7	Acid–Base Catalysis	112
8.8	Transition Metal Catalysis	113
8.9	Chiral Transition Metal Catalysis	115
8.10	Task-specific Ionic Liquids in Catalysis	117
	References	118

<b>Chapter 9 Inorganic Chemistry</b>	<b>121</b>
9.1 Introduction	121
9.2 Main Group Chemistry	121
9.3 Transition Metal Chemistry	124
9.4 Organometallic Compounds	125
9.5 Nuclear Chemistry	130
9.6 Nanoparticles	132
9.7 Carbon Nanotubes	133
9.8 Metal and Semiconductor Nanoparticles	134
9.9 Alloy Nanoparticles	136
9.10 Metal Oxide Nanoparticles	137
9.11 Other Nanoparticles	137
9.12 Microspheres	138
9.13 Sol–Gel Synthesis of Porous Materials	140
9.14 Ionothermal Synthesis of Porous Materials	141
References	143
<b>Chapter 10 General Organic Reactions</b>	<b>146</b>
10.1 Introduction	146
10.2 Aldol Condensation	146
10.3 Alkylation	148
10.4 Cracking	149
10.5 Cycloaddition	151
10.6 Debromination	152
10.7 Dimerization and Oligomerization	152
10.8 Electrophilic Reactions	155
10.9 Epoxidation	155
10.10 Esterification	157
10.11 Etherization	159
10.12 Halogenation	160
10.13 Hydroformylation	161
10.14 Hydrogenation	162
10.15 Hydrosilylation	166
10.16 Nitration of Aromatics	168
10.17 Nucleophilic Reactions	169
10.18 Olefin Metathesis	171
10.19 Oxidation	174
10.20 Peptide Synthesis	175
10.21 Photochemical Reactions	176
10.22 Polymerizations	179
References	183

<b>Chapter 11 Named Organic Reactions</b>	<b>188</b>
11.1 Baeyer–Villiger Oxidation	188
11.2 Baylis–Hillman Reaction	188
11.3 Beckmann Rearrangement	190
11.4 Diels–Alder Reaction	190
11.5 Friedel–Crafts Reactions	193
11.6 Grignard Reaction	197
11.7 Heck Reaction	198
11.8 Knoevenagel Condensation and Robinson Annulation	200
11.9 Mannich Reaction	202
11.10 Michael Addition	203
11.11 Sonogashira Coupling	205
11.12 Stille Coupling	206
11.13 Suzuki Cross-coupling	207
11.14 Swern Oxidation	208
11.15 Ullmann Coupling	209
11.16 Wacker Oxidation	210
11.17 Wittig Reaction	210
References	211
<b>Chapter 12 Biotechnology</b>	<b>214</b>
12.1 Introduction	214
12.2 Carbohydrate Solubility	214
12.3 Biomass Conversion	216
12.4 Enzyme Catalysis	218
12.5 Early Studies of Ionic Liquid–Enzyme Systems	220
12.6 Lipases	222
12.7 Proteases, Esterases and other Enzymes	223
12.8 Enantioselectivity and Regioselectivity	225
12.9 Biphasic Systems and Separations	227
References	229
<b>Chapter 13 Analysis</b>	<b>232</b>
13.1 Introduction	232
13.2 Chromatography	232
13.3 Capillary Electrophoresis	234
13.4 Sensors	236
13.5 Gas Sensors	236
13.6 Ion-selective Electrodes	239
13.7 Biosensors	240

13.8	Spectroscopy	241
13.9	Mass Spectrometry	242
	References	244
<b>Chapter 14</b>	<b>Applications</b>	<b>246</b>
14.1	Introduction	246
14.2	Synthesis of 2,5-Dihydrofuran	247
14.3	Difasol Process	248
14.4	BASIL Process	249
14.5	Storage of Hazardous Gases	250
14.6	Lubrication	251
14.7	Compressors	252
14.8	Energetic Materials and Propellants	253
14.9	Optical Immersion Fluids	255
14.10	Lunar Liquid Mirror Telescope	256
14.11	Thermometers	257
14.12	Antimicrobial Agents	259
14.13	Active Pharmaceutical Ingredients	260
14.14	Nucleoside-based Antiviral Drugs	261
14.15	Embalming and Tissue Preservation Fluids	264
	References	264
<b>Subject Index</b>		<b>266</b>