

Contents

Preface *xiii*

1 Synthesis and Properties 1

Karine De Oliveira Vigier and François Jérôme

- 1.1 Introduction 1
- 1.2 Synthesis 2
- 1.3 Properties 4
 - 1.3.1 Freezing Point (T_f) 4
 - 1.3.2 Density 5
 - 1.3.3 Viscosity 11
 - 1.3.4 Ionic Conductivity 16
 - 1.3.5 Polarity 19
 - 1.3.6 Surface Tension 19
- 1.4 Summary and Conclusions 21
- References 21

2 Structure and Implications 25

Oliver S. Hammond and Karen J. Edler

- 2.1 Introduction 25
- 2.2 Nanostructure of DES 26
 - 2.2.1 Complex Ion Model 26
 - 2.2.2 An Extended Hydrogen Bond Network Model: "Alphabet Soup" 27
 - 2.2.3 Non-cholinium DES 36
- 2.3 Conclusions and Implications 38
- Abbreviations 40
- References 40

3 Toxicity and Biodegradability of Deep Eutectic Solvents and Natural Deep Eutectic Solvents 43

Zhen Yang

- 3.1 Introduction 43
- 3.2 Toxicity to Microorganisms 44
 - 3.2.1 Toxicity to Bacteria 44

3.2.2	Toxicity to Other Microorganisms	47
3.3	Toxicity to Animals	48
3.3.1	<i>In Vitro</i> Toxicity Tests on Vertebrates and Invertebrates	48
3.3.2	Cytotoxicity	49
3.3.3	<i>In Vivo</i> Acute Toxicity Tests and Pharmacokinetics	53
3.4	Toxicity to Plants	55
3.5	Biodegradability	56
3.6	Summary and Conclusions	57
	Abbreviations	58
	References	59
4	Natural Deep Eutectic Solvents: From Their Discovery to Their Applications	61
	<i>Henni Vanda, Robert Verpoorte, Peter G. L. Klinkhamer, and Young H. Choi</i>	
4.1	Introduction	61
4.2	Natural Deep Eutectic Solvents Is a Concept Based on How Physicochemical Features Could Be Used for Biological Functions	63
4.3	Extraction and Solubilization of Non-water-Soluble Metabolites	66
4.4	Solvents for Macromolecules	69
4.4.1	Application of ILs and DES to Macromolecules	69
4.4.2	Recent NADES Application for DNA, RNA, and Proteins	70
4.5	Application to Enzyme Reactions	75
4.6	Pharmaceutical Applications	76
4.7	Perspective of NADES	76
	Abbreviations	79
	References	79
5	Hydrophobic Deep Eutectic Solvents	83
	<i>Samah E.E. Warrag and Maaïke C. Kroon</i>	
5.1	Introduction	83
5.2	Physiochemical Properties of Hydrophobic DESs	84
5.2.1	Density	85
5.2.2	Viscosity	86
5.3	Thermal Stability Window	86
5.4	Applications of Hydrophobic DESs	87
5.4.1	The Extraction of Fatty Acids and Biomolecules from Water	87
5.4.2	The Removal of Transition Metal Ions from Water	89
5.4.3	Impregnation in Membranes	90
5.4.4	The Removal of Pesticides from Water	90
5.4.5	CO ₂ Capture	90
5.5	Prediction of the Hydrophobic DESs Phase Behavior	91
5.5.1	The Use of PC-SAFT	91
5.6	Outlook and Recommendations	92
	Abbreviations	92
	References	93

6	Deep Eutectic Solvents: Exploring Their Role in Nature	95
	<i>Rita Craveiro, Francisca Mano, Alexandre Paiva, and Ana Rita C. Duarte</i>	
6.1	(Introduction) DES in Nature	95
6.2	Honey	97
6.2.1	Behind Beehive: How Honey Is Really Produced?	98
6.2.2	Honey and Its Properties	99
6.2.3	Honey as the First THEDES	99
6.3	Maple Syrup: How Is Maple Syrup Produced?	100
6.3.1	Maple Syrup Nutraceutical Value	101
6.3.2	Maple Syrup and NADES	102
6.4	Sugar Beet	102
6.5	Resurrection Plants	106
6.6	Summary and Conclusions	107
	Abbreviations	107
	Acknowledgments	108
	References	108
7	Organic Synthesis in DESs	111
	<i>Filippo M. Perna, Paola Vitale, and Vito Capriati</i>	
7.1	Introduction	111
7.2	DESs in Organocatalysis	112
7.3	DESs in the Synthesis of Heterocycles	116
7.3.1	Synthesis of Nitrogen- or Nitrogen- and Oxygen-Containing Rings in DESs	117
7.3.2	Synthesis of Thiophenes in DESs	119
7.3.3	Synthesis of Benzo-Condensed Rings in DESs	120
7.4	Multicomponent Reactions in DESs	123
7.4.1	Multicomponent Reactions in the Synthesis of Heterocycles	123
7.4.2	Synthesis of Betti Bases in DESs	128
7.4.3	Ugi and Passerini Reactions	128
7.5	Miscellaneous Transformations in DESs	129
7.6	Conclusion and Perspective	130
	Abbreviations	131
	References	132
8	DES as Catalyst	135
	<i>Mehran Shahiri-Haghighayegh and Najmedin Azizi</i>	
8.1	Introduction	135
8.2	DES Promoted Organic Transformations	136
8.2.1	Fischer Indole Synthesis	136
8.2.2	Carbon–Carbon Bond Formation	138
8.2.3	Synthesis of Pyrroles	141
8.2.4	Oxidation Reactions	141
8.2.5	“Green” Multicomponent Reactions	142
8.2.5.1	Isocyanide-Based MCRs	143
8.2.5.2	Mannich-Type Reactions	144

8.2.5.3	Biginelli Reaction	147
8.2.5.4	Synthesis of Chromene, Pyran, and Spiroindole Derivatives	149
8.2.5.5	Multicomponent Synthesis of Pyrrole and Pyrazole	149
8.2.5.6	Synthesis of Quinazoline	153
8.2.5.7	A3-Coupling Reaction	153
8.3	Desulfurization of Fuels	154
8.3.1	Olefin Alkylation of Thiophenic Sulfur	155
8.3.2	Oxidative Desulfurization of Fuels	156
8.4	Biodiesel Production	157
8.4.1	Transesterification of Triglycerides	158
8.4.2	Esterification of Free Fatty Acids	159
8.4.3	Hydrolysis/Dehydration of Carbohydrates	160
8.5	CO ₂ Chemical Fixation	161
8.6	Chemical Recycling of Polymers	163
8.7	Epoxy Resin Crosslinking	165
8.8	Supramolecular Macrocyclic Host Synthesis	166
8.9	Conclusion	166
	References	167
9	Metal-Promoted Organic Transformation in DES	171
	<i>Cristian Vidal and Joaquín García-Álvarez</i>	
9.1	Introduction	171
9.2	Design of New Synthetic Sustainable Organic Procedures Coupling Deep Eutectic Solvents and Highly-Polarized Organometallic Reagents (RLi and RMgX)	173
9.3	Transition-Metal-Catalyzed Organic Reactions in Deep Eutectic Solvents	177
9.3.1	Palladium Catalyzed C–C Coupling Reactions in DESs	177
9.3.2	Ruthenium Catalyzed Isomerization of Allylic Alcohols and Design of One-Pot Tandem Reactions in DESs	179
9.3.3	Gold Catalyzed Cycloisomerizations of Unsaturated Organic Substrates in DESs	180
9.4	Summary and Conclusions	181
	Abbreviations	182
	Acknowledgments	182
	References	183
10	Polymerizations	187
	<i>Josué D. Mota-Morales</i>	
10.1	Introduction	187
10.2	Deep Eutectic Solvents and Green Chemistry	188
10.3	The Role of Deep Eutectic Solvents in Polymerizations	189
10.3.1	Polymerizations Carried Out in Deep Eutectic Solvents	189
10.3.2	Polymerization of Monomers Containing Deep Eutectic Solvents: DES Monomers	191

10.3.3	DES as Cosolvents and Auxiliaries in Polymerizations	192
10.3.4	Cooperative Hydrogen Bonding Network of Water Added to DESs	194
10.4	Mechanisms of Polymerization Explored	194
10.4.1	Polycondensation	194
10.4.2	Free-Radical Polymerization	197
10.4.3	Ring Opening Polymerization	207
10.4.4	Other Mechanisms of Polymerizations	209
10.5	Outlook and Future Directions	210
	Abbreviations	212
	References	212
11	Extraction of Bioactive Compounds	217
	<i>Mohamad H. Zainal-Abidin, Maan Hayyan, Gek C. Ngoh, Won F. Wong, and Adeen Hayyan</i>	
11.1	Introduction	217
11.2	The Main Features of DESs as an Extractive Agent	218
11.2.1	Effect of Water Addition on Extraction Efficiency	219
11.3	DESs in the Bioactive Compound Extractions	221
11.3.1	Phenolic Compounds	222
11.3.1.1	Flavonoid Compounds	225
11.3.2	Polysaccharides	226
11.3.3	Proteins	227
11.3.4	Hydrophobic Compounds	228
11.4	Summary	230
	Abbreviations	230
	References	231
12	Processing of Biomass in Deep Eutectic Solvents	235
	<i>Miao Zuo, Xianhai Zeng, Yong Sun, Xing Tang, and Lu Lin</i>	
12.1	Introduction	235
12.2	Chemical Process of Products Extraction from Biomass in DESs	235
12.2.1	Extraction and Solubility of Lignocellulose in DESs	235
12.2.2	Value-Added Products Extraction from Biomass in DESs	238
12.3	Modification of Cellulose in DESs	240
12.4	Catalytic Conversion of Carbohydrates in DESs	242
12.4.1	Catalytic Conversion of Carbohydrates in Neat DESs	242
12.4.2	HMF Production from Carbohydrates in Bio-Based DESs	244
12.4.3	Carbohydrates Dehydration in Biphasic DES/Organic Solvent Systems	246
12.4.4	Carbohydrates Dehydration to Other Value-Added Products in DESs	249
12.5	Conclusions and Prospects	251
	Abbreviations	252
	Acknowledgments	252
	References	253

13	Enzyme Catalysis: In DES, with DES, and in the Presence of DES	257
	<i>Pablo Domínguez de María, Nadia Guajardo, and Selin Kara</i>	
13.1	DESs as “Non-Conventional Media” and “Non-Conventional Solutions” for Biocatalysis	257
13.2	Hydrolases and Deep Eutectic Solvents	259
13.3	Oxidoreductases and Deep Eutectic Solvents	264
13.4	Other Biocatalytic Concepts in Deep Eutectic Solvents	266
13.5	Conclusions	267
	Abbreviations	268
	References	268
14	Nanoscale and Functional Materials	273
	<i>Diego A. Alonso, Alejandro Baeza, Rafael Chinchilla, Cecilia Gómez, and Isidro M. Pastor</i>	
14.1	Introduction	273
14.2	Nanoparticulated Materials	274
14.3	Nanofilms and Nanolayers	282
14.4	Carbonaceous Materials	283
14.5	Porous Materials	287
14.6	DNA Manipulation	290
14.7	Summary and Conclusions	291
	Abbreviations	292
	References	292
15	Carbon Dioxide Capture	297
	<i>Yingying Zhang, Xiaohua Lu, and Xiaoyan Ji</i>	
15.1	Introduction	297
15.2	Properties of DESs	299
15.2.1	Thermophysical Properties	299
15.2.1.1	Gas Solubility	299
15.2.1.2	Viscosity	305
15.2.1.3	Molar Heat Capacity	309
15.2.2	Kinetic Property	312
15.3	Screening and Evaluation of DESs for CO ₂ Separation	313
15.3.1	Property-Based Method	313
15.3.2	Thermodynamic Analysis-Based Method	313
15.3.3	Process Simulation-Based Method	314
15.4	Further Conversion with DESs	314
15.5	Conclusions	314
	Abbreviations	315
	References	316
16	DES-Mediated Approaches Toward Green Analytical Chemistry	321
	<i>Federico J.V. Gomez, Magdalena Espino, Maria de los A. Fernández, Joana Boiteux, and María F. Silva</i>	
16.1	Introduction	321
16.2	Extraction Techniques and Deep Eutectic Solvents	323

16.2.1	Ultrasound Assisted Extraction (UAE)	324
16.2.2	Microwave Assisted Extraction (MAE)	325
16.2.3	Liquid Phase Microextraction (LPME)	325
16.2.4	Solid Phase Microextraction (SPME)	326
16.3	Separation Techniques and DES	326
16.3.1	Gas Chromatography and DES	327
16.3.2	Liquid Chromatography and DES	327
16.3.3	Capillary Electrophoresis and DES	328
16.4	DES Detection Techniques Compatibility	328
16.5	Future Trends and Challenges for Green Solvents in Analytical Chemistry	330
	Abbreviations	331
	Acknowledgments	332
	References	332
17	Electrochemistry	335
	<i>Zhimin Xue, Wancheng Zhao, and Tiancheng Mu</i>	
17.1	Introduction	335
17.2	Conductivity	336
17.3	Electrochemical Stability	347
17.4	Electrochemical Applications	350
17.4.1	Electrodeposition	350
17.4.2	Electropolishing	357
17.5	Summary and Conclusions	359
	Abbreviations	359
	Acknowledgments	360
	References	360
	Index	363