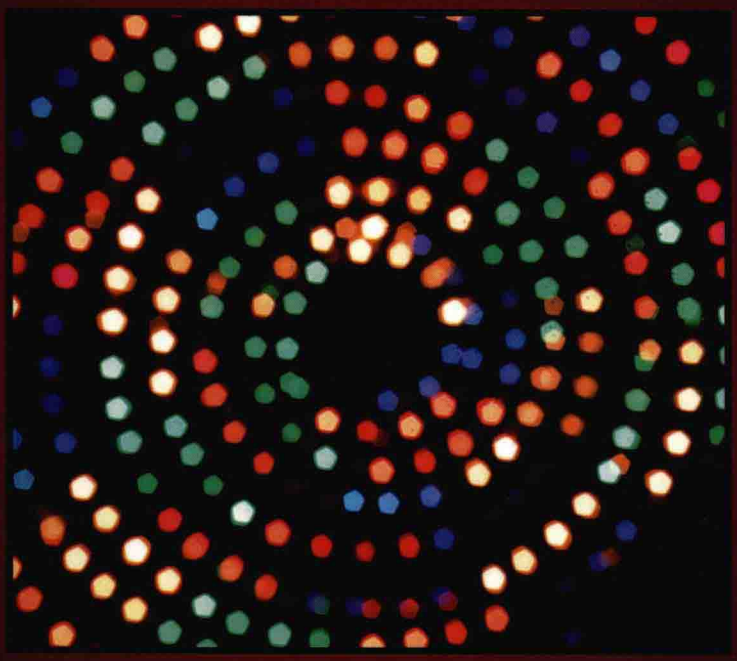
Ionic Liquids UnCOILed

Critical Expert Overviews



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WILEY

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IONIC LIQUIDS UNCOILED

PREFACE

So, why the strange title for this book? Is this just a book of conference proceedings based on lectures at COIL? How is this book different from the series of volumes that were edited with Prof. Robin D. Rogers based on symposia we had organised at American Chemical Society (ACS) meetings? We will attempt here to answer these questions, and others, and hence explain the philosophy behind this book.

COIL (Congress on Ionic Liquids) was a concept that originally arose in discussions with DeChema, following on from a meeting about the Green Solvents series of conferences, which have traditionally been held in Germany. It was noticed that the number of submitted papers on ionic liquids surpassed the total of all the other papers combined. At that time, the only international meeting on ionic liquids had been a NATO Workshop, held in Crete in 2000 (Rogers, R.D., Seddon, K.R., and Volkov, S. (eds.), *Green industrial applications of ionic liquids*, NATO Science Series II: Mathematics, Physics and Chemistry, Vol. 92, Kluwer, Dordrecht, 2002). This was correctly interpreted as a need for a truly dedicated international meeting on ionic liquids, and so COIL was born. With the invaluable support of DeChema, the first meeting was held in Salzburg (literally, and appropriately, "Salt Castle"), and it has since moved around the world biannually, in a carefully planned progression. These meetings have been a resounding success, and their timeline is given on the opposite page. It is, unquestionably, the foremost forum for showcasing and discussing the latest advances in ionic liquids. However, we, and others, resisted the temptation to produce proceedings volumes. Although having a certain value as a time capsule, such volumes date quickly, and individual chapters are poorly cited (as they usually appear around the same time in the primary journals). Nevertheless, taken together, the COIL speakers have been a remarkable group of chemists, chemical engineers, biochemists, and biologists. Surely such a talented assembly of scientists could make a valuable contribution, *en masse*, to the published literature. And so this volume, *Ionic Liquids UnCOILed*, slowly emerged from our collective mind: "UnCOILed" because, although every principal author has presented their work as COIL lectures, the chapter content in this book has never been presented there. We wrote to each of our selected authors (and, amazingly, only one turned us down!), and set them a difficult challenge. The letter we sent out included the following text: "The concept is to select the key speakers from COIL-1, COIL-2 and COIL-3 and invite them to write critical reviews on specific areas of ionic liquid chemistry.

The area we have selected for you is [...]. It is important to emphasise that these are meant to be critical reviews. We are not looking for comprehensive coverage, but insight, appreciation and prospect. We want the type of review which can be read to give a sense of importance and scope of the area, highlighting this by the best published work and looking for the direction in which the field is moving. We would also like the problems with the area highlighting, for example, poor experimental technique, poor selection of liquids, and variability of data. We hope you would like to be involved in this project, as we believe these books will define the field for the next few years." Indeed, we felt rather like Division Seven, contacting the Impossible Missions Force (in the original, more cerebral, TV series, not the recent films!), "Your mission [...] should you decide to accept it . . ." However, to the best of our knowledge, the emails did not "self-destruct in five seconds," and the acceptance rate was beyond our best expectations. We also issued guidance as to which abbreviations to use, and so there is concordance between every chapter (unlike a recent book, which contained over 25 different abbreviations for a single ionic liquid!).

The quality and size of the reviews that we received meant that we had to revert to Wiley and ask permission to produce not one, but three books! Wiley generously agreed. Thus, this will be the first of three volumes. The following ones, at six monthly intervals, will be *Ionic Liquids Further UnCOILed* and *Ionic Liquids Completely UnCOILed*. All will contain overviews of the same critical nature.

We look forward to the response of our readership (we can be contacted at quill@qub.ac.uk). It is our view that, in the second decade of the 21st century, reviews that merely regurgitate a list of all papers on a topic, giving a few lines or a paragraph (often the abstract!) to each one, have had their day. Five minutes with an online search engine will provide that information. The value of a review lies in the expertise and insight of the reviewer—and their willingness to share it with the reader. It takes moral courage to say "the work of [...] is irreproducible, or of poor quality, or that the conclusions are not valid"—but in a field expanding at the prestigious rate of ionic liquids, it is essential to have this honest feedback. Otherwise, errors are propagated. Papers still appear using hexafluorophosphate or tetrafluoroborate ionic liquids for synthetic or catalytic chemistry, and calculations on "ion pairs" are still being used to rationalise liquid state properties! We trust that this volume, containing 11 excellently perceptive reviews, will help guide and secure the future of ionic liquids.

NATALIA V. PLECHKOVA
KENNETH R. SEDDON

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This volume is a collaborative effort. We, the editors, have our names emblazoned on the cover, but the book would not exist in its present form without support from many people. First, we thank our authors for producing such splendid, critical chapters, and for their open responses to the reviewers' comments and to editorial suggestions. We are also indebted to our team of expert reviewers, whose comments on the individual chapters were challenging and thought provoking, and to Ian Gibson for his input to the cover design. The backing from the team at Wiley, led by Dr. Arza Seidel, has been fully appreciated—it is always a joy to work with such a professional group of people. Finally, this book would never have been published without the unfailing, enthusiastic support from Deborah Poland, Sinead McCullough, and Maria Diamond, whose patience and endurance never cease to amaze us.

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ABBREVIATIONS

Ionic Liquids

GNCS	guanidinium thiocyanate
[HI-AA]	hydrophobic derivatised amino acid
IL	ionic liquid
poly(RTILs)	polymerisable room temperature ionic liquids
$[PSpy]_3[PW]$	$[1\text{-}(3\text{-sulfonic acid})propylpyridinium]_3[PW_{12}O_{40}]\cdot 2H_2O$

Cations

$[1\text{-}C_m\text{-}3\text{-}C_n im]^+$	1,3-dialkylimidazolium
$[C_n mim]^+$	1-alkyl-3-methylimidazolium
$[Hmim]^+$	1-methylimidazolium
$[C_1 mim]^+$	1,3-dimethylimidazolium
$[C_2 mim]^+$	1-ethyl-3-methylimidazolium
$[C_3 mim]^+$	1-propyl-3-methylimidazolium
$[C_4 mim]^+$	1-butyl-3-methylimidazolium
$[C_5 mim]^+$	1-pentyl-3-methylimidazolium
$[C_6 mim]^+$	1-hexyl-3-methylimidazolium
$[C_7 mim]^+$	1-heptyl-3-methylimidazolium
$[C_8 mim]^+$	1-octyl-3-methylimidazolium
$[C_9 mim]^+$	1-nonyl-3-methylimidazolium
$[C_{10} mim]^+$	1-decyl-3-methylimidazolium
$[C_{11} mim]^+$	1-undecyl-3-methylimidazolium
$[C_{12} mim]^+$	1-dodecyl-3-methylimidazolium
$[C_{13} mim]^+$	1-tridecyl-3-methylimidazolium
$[C_{14} mim]^+$	1-tetradecyl-3-methylimidazolium
$[C_{15} mim]^+$	1-pentadecyl-3-methylimidazolium
$[C_{16} mim]^+$	1-hexadecyl-3-methylimidazolium
$[C_{17} mim]^+$	1-heptadecyl-3-methylimidazolium
$[C_{18} mim]^+$	1-octadecyl-3-methylimidazolium
$[C_8 C_3 im]^+$	1-octyl-3-propylimidazolium
$[C_{12} C_{12} im]^+$	1,3-bis(dodecyl)imidazolium
$[C_4 dmim]^+$	1-butyl-2,3-dimethylimidazolium
$[C_4 C_1 mim]^+$	1-butyl-2,3-dimethylimidazolium

$[C_6C_{7O1}im]^+$	1-hexyl-3-(heptyloxymethyl)imidazolium
$[C_4vim]^+$	3-butyl-1-vinylimidazolium
$[D_{mvim}]^+$	1,2-dimethyl-3-(4-vinylbenzyl)imidazolium
$[(allyl)mim]^+$	1-allyl-3-methylimidazolium
$[P_nmim]^+$	polymerisable 1-methylimidazolium
$[C_2mmor]^+$	1-ethyl-1-methylmorpholinium
$[C_4py]^+$	1-butylpyridinium
$[C_4m_\beta py]^+$	1-butyl-3-methylpyridinium
$[C_4m_\gamma py]^+$	1-butyl-4-methylpyridinium
$[C_4mpyr]^+$	1-butyl-1-methylpyrrolidinium
$[C_2C_6pip]^+$	1-ethyl-1-hexylpiperidinium
$[C_8quin]^+$	1-octylquinolinium
$[H_2NC_2H_4py]^+$	1-(1-aminoethyl)-pyridinium
$[H_2NC_3H_6mim]^+$	1-(3-aminopropyl)-3-methylimidazolium
$[Hnmp]^+$	1-methyl-2-pyrrolidonium
$[N_{1\,1\,2\,2OH}]^+$	ethyl(2-hydroxyethyl)dimethylammonium
$[N_{1\,1\,1\,4}]^+$	trimethylbutylammonium
$[N_{4\,4\,4\,4}]^+$	tetrabutylammonium
$[N_{6\,6\,6\,14}]^+$	trihexyl(tetradecyl)ammonium
$[P_{2\,2\,2(1O1)}]$	triethyl(methoxymethyl)phosphonium
$[P_{4\,4\,4\,3a}]^+$	(3-aminopropyl)tributylphosphonium
$[P_{6\,6\,6\,14}]^+$	trihexyl(tetradecyl)phosphonium
$[S_{2\,2\,2}]^+$	triethylsulfonium

ANIONS

$[Ala]^-$	alaninate
$[\beta Ala]^-$	β-alaninate
$[Arg]^-$	arginate
$[Asn]^-$	asparaginate
$[Asp]^-$	aspartate
$[BBB]^-$	bis[1,2-benzenediolato(2-)-*O,O′*]borate
$[C_1CO_2]^-$	ethanoate
$[C_1SO_4]^-$	methylsulfate
$[CTf_3]^-$	tris{(trifluoromethyl)sulfonyl}methanide
$[Cys]^-$	cysteinate
$[FAP]^-$	tris(perfluoroalkyl)trifluorophosphate
$[Gln]^-$	glutaminate
$[Glu]^-$	glutamate
$[Gly]^-$	glycinate
$[His]^-$	histidinate
$[Ile]^-$	isoleucinate
$[lac]^-$	lactate
$[Leu]^-$	leucinate

$[Lys]^-$	lysinate
$[Met]^-$	methionate
$[Nle]^-$	norleucinate
$[NPf_2]^-$	bis{(pentafluoroethyl)sulfonyl}amide
$[NTf_2]^-$	bis{(trifluoromethyl)sulfonyl}amide
$[O_2CC_1]^-$	ethanoate
$[O_3SOC_2]^-$	ethylsulfate
$[OMs]^-$	methanesulfonate (mesylate)
$[OTf]^-$	trifluoromethanesulfonate
$[OTs]^-$	4-toluenesulfonate, $[4\text{-}CH_3C_6H_4SO_3]^-$ (tosylate)
$[Phe]^-$	phenylalaninate
$[Pro]^-$	prolinate
$[Ser]^-$	serinate
$[Suc]^-$	succinate
$[Thr]^-$	threoninate
$[Trp]^-$	tryphtophanate
$[Tyr]^-$	tyrosinate
$[Val]^-$	valinate

TECHNIQUES

AES	Auger electron spectroscopy
AFM	atomic force microscopy
ANN	associative neural network
ARXPS	angle resolved X-ray photoelectron spectroscopy
ATR-IR	attenuated total reflectance infrared spectroscopy
BPNN	back-propagation neural network
CCC	counter-current chromatography
CE	capillary electrophoresis
CEC	capillary electrochromatography
COSMO-RS	**CO**nductorlike**S**creening**MO**del for Real Solvents
COSY	**CO**rrelation **S**pectroscop**Y**
CPCM	conductor-like polarisable continuum model
CPMD	Car–Parrinello molecular dynamics
DFT	density functional theory
DRS	direct recoil spectroscopy
DSC	differential scanning calorimetry
DSSC	dye-sensitised solar cell
ECSEM	electrochemical scanning electron microscopy
EC-XPS	electrochemical X-ray photoelectron spectroscopy
EFM	effective fragment potential method
EI	electron ionisation
EOF	electro-osmotic flow
EPSR	empirical potential structure refinement

ES	electrospray mass spectrometry
ESI–MS	electrospray ionisation mass spectrometry
EXAFS	extended X-ray absorption fine structure
FAB	fast atom bombardment
FMO	fragment molecular orbital method
GC	gas chromatography
GGA	generalized gradient approximations
GLC	gas–liquid chromatography
GSC	gas–solid chromatography
HM	heuristic method
HPLC	high performance liquid chromatography
HREELS	high resolution electron energy loss spectroscopy
IGC	inverse gas chromatography
IR	infrared spectroscopy
IRAS	infrared reflection absorption spectroscopy
IR-VIS SFG	infrared visible sum frequency generation
ISS	ion scattering spectroscopy
L-SIMS	liquid secondary ion mass spectrometry
MAES	metastable atom electron spectroscopy
MALDI	matrix-assisted laser desorption
MBSS	molecular beam surface scattering
MIES	metastable impact electron spectroscopy
MLR	multi-linear regression
MM	molecular mechanics
MS	mass spectrometry
NMR	nuclear magnetic resonance
NR	neutron reflectivity
PDA	photodiode array detection
PES	photoelectron spectroscopy
PPR	projection pursuit regression
QM	quantum mechanics
QSAR	quantitative structure–activity relationship
QSPR	quantitative structure–property relationship
RAIRS	reflection absorption infrared spectroscopy
RI	refractive index
RNN	recursive neural network
RP-HPLC	reverse phase-high performance liquid chromatography
SANS	small angle neutron scattering
SEM	scanning electron microscopy
SFA	surfaces forces apparatus
SFC	supercritical fluid chromatography
SFG	sum frequency generation
SFM	systematic fragmentation method
SIMS	secondary ion mass spectrometry
STM	scanning tunnelling microscopy

SVN	support vector network
TEM	tunnelling electron microscopy
TGA	thermogravimetric analysis
TLC	thin layer chromatography
TPD	temperature programmed desorption
UHV	ultra-high vacuum
UPLC	ultra-pressure liquid chromatography
UPS	ultraviolet photoelectron spectroscopy
UV	ultraviolet
UV-Vis	ultraviolet-visible
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction
XRR	X-ray reflectivity

MISCELLANEOUS

Å	1 Ångstrom = 10^{-10} m
ACS	American Chemical Society
ATPS	aqueous two-phase system
BE	binding energy
BILM	bulk ionic liquid membrane
b.pt.	boiling point
BSA	bovine serum albumin
BT	benzothiophene
calc.	calculated
CB	Cibacron Blue 3GA
CE	crown ether
CLM	charge lever momentum
CMC	critical micelle concentration
CMPO	octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide
COIL	Congress on Ionic Liquids
CPU	central processing unit
d	doublet (NMR)
D°_{298}	bond energy at 298 K
2D	two-dimensional
3D	three-dimensional
DBT	dibenzothiophene
DC18C6	dicyclohexyl-18-crown-6
4,6-DMDBT	4,6-dimethyldibenzothiophene
DMF	dimethylmethanamide (dimethylformamide)
2DOM	two-dimensional ordered macroporous
3DOM	three-dimensional ordered macroporous
DOS	density of states

DPC	diphenylcarbonate
DRA	drag-reducing agent
DSSC	dye-sensitised solar cell
E	enrichment
EDC	extractive distillation column
EOR	enhanced oil recovery
EPA	Environmental Protection Agency
EPSR	empirical potential structure refinement
eq.	equivalent
FCC	fluid catalytic cracking
FFT	fast Fourier transform
FIB	focused ion beam
FSE	full-scale error
ft	foot
GDDI	generalised distributed data interface
HDS	hydrodesulfurisation
HEMA	2-(hydroxyethyl) methacrylate
HOMO	highest occupied molecular orbital
HOPG	highly oriented pyrolytic graphite
HV	high vacuum
IgG	immunoglobulin G
IPBE	ion pair binding energy
ITO	indium-tin oxide
IUPAC	International Union of Pure and Applied Chemistry
J	coupling constant (NMR)
LCST	lower critical separation temperature
LLE	liquid–liquid equilibria
LUMO	lowest unoccupied molecular orbital
m	multiplet (NMR)
M	molar concentration
MBI	1-methylbenzimidazole
MCH	methylcyclohexane
MD	molecular dynamics
MDEA	methyl diethanolamine; bis(2-hydroxyethyl)methylamine
MEA	monoethanolamine; 2-aminoethanol
MFC	minimal fungicidal concentrations
MIC	minimal inhibitory concentrations
MNDO	modified neglect of differential overlap
m.pt.	melting point
3-MT	3-methylthiophene
MW	molecular weight
m/z	mass-to-charge ratio
NBB	1-butylbenzimidazole
NCA	*N*-carboxyamino acid anhydride
NES	New Entrepreneur Scholarship