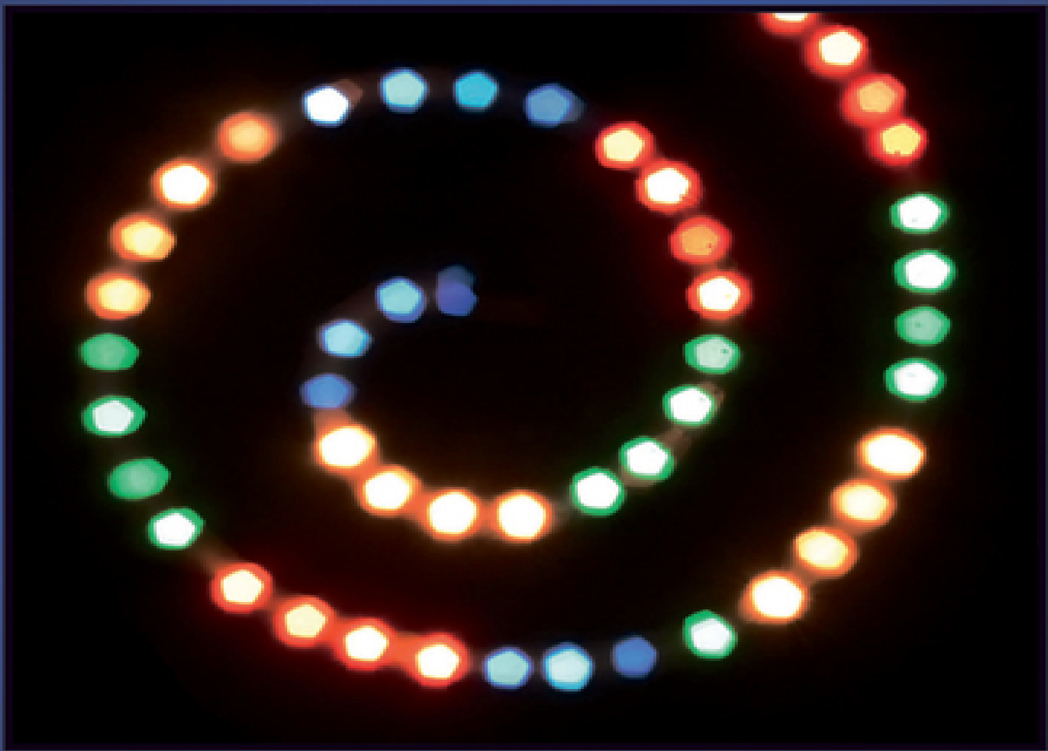
Ionic Liquids Further UnCOILed

Critical Expert Overviews



Edited by

NATALIA V. PLECHKOVA
KENNETH R. SEDDON

WILEY

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COIL Conferences

COIL-1	Salzburg	Austria	2005
COIL-2	Yokohama	Japan	2007
COIL-3	Cairns	Australia	2009
COIL-4	Washington	USA	2011
COIL-5	Algarve	Portugal	2013
COIL-6	Jeju Island	Korea	2015
COIL-7	Ottawa*	Canada	2017
COIL-8	Belfast*	UK	2019

* Precise location still to be confirmed.

Preface

This is the second of three volumes of critical overviews of the key areas of ionic liquid chemistry. The first volume is entitled *Ionic Liquids UnCOILed* (Wiley 2013), the current volume is *Ionic Liquids Further UnCOILed*, and the final volume, called *Ionic Liquids Completely UnCOILed*, will be published later this year. The history and rationale behind this trilogy was explained in the preface to the first volume, and so will not be repeated here.

Instead, we will use this space to expand on the subtitle, constant for all three volumes: Critical Expert Overviews.

critical, adjective

1. Involving or exercising careful judgement or judicious evaluation

2. Of decisive importance in relation to an issue; decisive, crucial

Critical has two, rather different, meanings—both are implied in the subtitle of this book. These reviews are both decisively important *and* written by top world experts (hence the second adjective), exercising the judicious evaluation that they are uniquely qualified to do.

overview, noun

1. A general survey; a comprehensive review of facts or ideas; a concise statement or outline of a subject. Also: a broad or overall view of a subject.

2. A view from above.

This book includes eleven critical expert overviews of differing aspects of ionic liquids. We look forward to the response of our readers (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. Such reviews belong with the slide rule, the fax machine, and the printed journal—valuable in their day, but of little value now. 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 this volume, containing eleven excellently perceptive reviews, will help guide and secure the future of ionic liquids.

Natalia V. Plechkova
Kenneth R. Seddon

Acknowledgements

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. Firstly, 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 producing the central image on the front cover. 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 and Sinead McCullough, whose patience and endurance never cease to amaze us.

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Abbreviations

Ionic Liquids

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

Cations

$[(allyl)mim]^+$	1-allyl-3-methylimidazolium
$[1\text{-}C_m\text{-}3\text{-}C_n im]^+$	1,3-dialkylimidazolium
$[C_2 im]^+$	1-ethylimidazolium
$[C_1 mim]^+$	1,3-dimethylimidazolium
$[C_2 mim]^+$	1-ethyl-3-methylimidazolium
$[C_3 mim]^+$	1-propyl-3-methylimidazolium
$[{}^iC_3 mim]^+$	1-isopropyl-3-methylimidazolium
$[C_4 mim]^+$	1-butyl-3-methylimidazolium
$[i\text{-}C_4 mim]^+$	1-isobutyl-3-methylimidazolium
$[s\text{-}C_4 mim]^+$	1-secbutyl-3-methylimidazolium
$[{}^tC_4 mim]^+$	1-tertbutyl-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
$[C_nmim]^+$	1-alkyl-3-methylimidazolium
$[C_1C_1mim]^+$	1,2,3-trimethylimidazolium
$[C_2C_1mim]^+$	1-ethyl-2,3-dimethylimidazolium
$[C_3C_1mim]^+$	1-propyl-2,3-dimethylimidazolium
$[C_8C_3im]^+$	1-octyl-3-propylimidazolium
$[C_{12}C_{12}im]^+$	1,3-bis(dodecyl)imidazolium
$[C_1OC_2mim]^+$	1-(2-methoxyethyl)-3-methyl-3H-imidazolium
$[C_4dmim]^+$	1-butyl-2,3-dimethylimidazolium
$[C_4C_1mim]^+$	1-butyl-2,3-dimethylimidazolium
$[C_6C_7O_1im]^+$	1-hexyl-3-(heptyloxymethyl)imidazolium
$[C_2F_3mim]^+$	1-trifluoroethyl-3-methylimidazolium
$[C_4vim]^+$	3-butyl-1-vinylimidazolium
$[D_{mvim}]^+$	1,2-dimethyl-3-(4-vinylbenzyl)imidazolium
$[C_2mmor]^+$	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
$[C_6(dma)_{\gamma}py]^+$	1-hexyl-4-dimethylaminopyridinium
$[C_1C_3pip]^+$	1-methyl-1-propylpiperidinium
	1-ethyl-1-hexylpiperidinium

$[C_2C_6pip]^+$	
$[C_8quin]^+$	1-octylquinolinium
$[DMPhim]^+$	1,3-dimethyl-2-phenylimidazolium
$[EtNH_3]^+$	ethylammonium
$[Hmim]^+$	1-methylimidazolium
$[H_2NC_2H_4py]^+$	1-(1-aminoethyl)-pyridinium
$[H_2NC_3H_6mim]^+$	1-(3-aminopropyl)-3-methylimidazolium
$[Hnmp]^+$	1-methyl-2-pyrrolidonium
$[HN_{2\ 2\ 2}]^+$	triethylammonium
$[N_{1\ 1\ 1\ 2OH}]^+$	cholinium
$[N_{1\ 1\ 2\ 2OH}]^+$	ethyl(2-hydroxyethyl)dimethylammonium
$[N_{1\ 1\ 1\ 4}]^+$	trimethylbutylammonium
$[N_{1\ 4\ 4\ 4}]^+$	methyltributylammonium
$[N_{1\ 8\ 8\ 8}]^+$	methyltrioctylammonium
$[N_{4\ 4\ 4\ 4}]^+$	tetrabutylammonium
$[N_{6\ 6\ 6\ 14}]^+$	trihexyl(tetradecyl)ammonium
$[NR_3H]^+$	trialkylammonium
$[P_{2\ 2\ 2(1O1)}]^+$	triethyl(methoxymethyl)phosphonium
$[P_{4\ 4\ 4\ 3a}]^+$	(3-aminopropyl)tributylphosphonium
$[P_{6\ 6\ 6\ 14}]^+$	trihexyl(tetradecyl)phosphonium
$[P_{8\ 8\ 8\ 14}]^+$	tetradecyl(trioctyl)phosphonium
$[P_n mim]^+$	polymerisable 1-methylimidazolium
$[PhCH_2eim]^+$	1-benzyl-2-ethylimidazolium
$[pyH]^+$	pyridinium
$[S_{2\ 2\ 2}]^+$	triethylsulfonium

Anions

$[Ala]^-$	alaninate
$[\beta Ala]^-$	β-alaninate
	tetra(hexafluoroisopropoxy)aluminate(III)

$[Al(hfip)_4]^-$	
$[Arg]^-$	arginate
$[Asn]^-$	asparaginate
$[Asp]^-$	asparatinate
$[BBB]^-$	bis[1,2-benzenediolato(2-)-*O,O*']borate
$[C_1CO_2]^-$	ethanoate
$[C_1SO_4]^-$, $[O_3SOC_1]^-$	methyl sulfate
$[C_8SO_4]^-$, $[O_3SOC_8]^-$	octyl sulfate
$[C_nSO_4]^-$	alkyl sulfate
$[(C_n)(C_m)SO_4]^-$	asymmetrical dialkyl sulfate
$[(C_n)_2SO_4]^-$	symmetrical dialkyl sulfate
$[CTf_3]^-$	tris{(trifluoromethyl)sulfonyl}methanide
$[Cys]^-$	cysteinate
$[FAP]^-$	tris(perfluoroalkyl)trifluorophosphate
$[Gln]^-$	glutaminate
$[Glu]^-$	glutamate
$[Gly]^-$	glycinate anion
$[His]^-$	histidinate
$[Ile]^-$	isoleucinate
$[lac]^-$	lactate
$[Leu]^-$	leucinate
$[Lys]^-$	lysinate
$[Met]^-$	methionate
$[Nle]^-$	norleucinate
$[NPf_2]^-$, $[BETI]^-$	bis{(pentafluoroethyl)sulfonyl}amide
$[NTf_2]^-$, $[TFSI]^-$	bis{(trifluoromethyl)sulfonyl}amide
$[O_2CC_1]^-$	ethanoate
$[O_3SOC_2]^-$, $[O_3SOC_2]^-$	ethylsulfate
$[OMs]^-$	methanesulfonate (mesylate)
$[ONf]^-$	perfluorobutylsulfonate
$[OTf]^-$	trifluoromethanesulfonate

$[OTs]^-$	4-toluenesulfonate, $[4\text{-}CH_3C_6H_4SO_3]^-$ (tosylate)
$[Phe]^-$	phenylalaninate
$[Pro]^-$	prolinate
$[Ser]^-$	serinate
$[Suc]^-$	succinate
$[tfpb]^-$	tetrakis(3,5-bis(trifluoromethyl)phenyl)borate
$[Thr]^-$	threoninate
$[Tos]^-$	tosylate
$[Trp]^-$	tryphtophanate
$[Tyr]^-$	tyrosinate
$[Val]^-$	valinate

Techniques

AES	Auger electron spectroscopy
AFM	atomic force microscopy
AMBER	assisted model building with energy refinement
ANN	associative neural network
ARXPS	angle resolved X-ray photoelectron spectroscopy
ASM	Associated-Solution Model
ATR-IR	attenuated total reflectance infrared spectroscopy
BPNN	back-propagation neural network
CADM	computer-aided design modelling
CC	Cole–Cole model
CCC	counter-current chromatography
CD	Cole–Davidson model
CE	capillary electrophoresis
CEC	capillary electrochromatography
CHARMM	Chemistry at HARvard Molecular Mechanics
COSMO-RS	**CO**nductor-like**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
DMH	dimethylhexene
DRS	dielectric relaxation spectroscopy
DSC	differential scanning calorimetry
ECSEM	electrochemical scanning electron microscopy
EC-XPS	electrochemical X-ray photoelectron spectroscopy
EFM	effective fragment potential method

EI	electron ionisation
EMD	equilibrium molecular dynamics
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
FIR	far-infrared spectroscopy
FMO	fragment molecular orbital method
FTIR	Fourier transform infrared spectroscopy
GAMESS	general atomic and molecular electronic structure system
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
MC	Monte Carlo
MD	molecular dynamics
MIES	metastable impact electron spectroscopy
MLR	multi-linear regression
MM	molecular mechanics
MS	mass spectrometry
NEMD	non-equilibrium molecular dynamics
NMR	nuclear magnetic resonance
NR	neutron reflectivity
NRTL	non-random two liquid
OPLS	optimized potentials for liquid simulations
PCM	polarisable continuum model
PDA	photodiode array detection
PES	photoelectron spectroscopy
PGSE-NMR	pulsed-gradient spin-echo

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
RNEMD	reverse non-equilibrium molecular dynamics
RNN	recursive neural network
RP-HPLC	reverse phase high-performance liquid chromatography
RST	regular solution theory
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
soft-SAFT	soft statistical associating fluid theory
STM	scanning tunnelling microscopy
SVN	support vector network
TEM	tunnelling electron microscopy
TGA	thermogravimetric analysis
THz-TDS	terahertz time-domain spectroscopy
TLC	thin layer chromatography
tPC-PSAFT	truncated perturbed chain polar statistical associating fluid theory
TPD	temperature programmed desorption
UHV	ultra-high vacuum
UNIFAC	UNIversal Functional Activity Coefficient
UNIQUAC	UNIversal QUAsiChemical
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
ATMS	acetyltrimethylsilane
ATPS	aqueous two-phase system

BASF™	Badische Anilin- und Soda-Fabrik
BASIL	Biphasic Acid Scavenging utilizing Ionic Liquids
BE	binding energy
BILM	bulk ionic liquid membrane
BNL	Brookhaven National Laboratory
b.pt.	boiling point
BSA	bovine serum albumin
BT	benzothiophene
calc.	calculated
CB	Cibacron Blue 3GA
CCD	charge coupled device
CE	crown ether
CEES	2-chloroethyl ethyl sulphide
CFC MC	“continuous fractional component” Monte Carlo
CLM	charge lever momentum
CMC	critical micelle concentration
CMPO	octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide
$[C_nMeSO_4]$	alkyl methyl sulfate
CNTs	carbon nanotubes
COIL	Congress on Ionic Liquids
CPU	central processing unit
CWAs	chemical warfare agents
d	doublet (NMR)
$D°_{298}$	bond energy at 298 K
2D	two-dimensional
3D	three-dimensional
DBT	dibenzothiophene
DC	direct current
DC18C6	dicyclohexyl-18-crown-6
DF	Debye and Falkenhagen
DH	Debye–Hückel
DIIPA	diisopropylamine
4,6-DMDBT	4,6-dimethyldibenzothiophene
DMF	dimethylmethanamide (dimethylformamide)
DNA	deoxyribonucleic acid
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
EE	expanded ensemble approach
EOR	enhanced oil recovery
EoS	equation of state
EPA	Environmental Protection Agency
EPSR	empirical potential structure refinement
eq.	equivalent
FCC	fluid catalytic cracking
FFT	fast Fourier transform
FIB	focussed ion beam
FSE	full-scale error
ft	foot
GDDI	generalised distributed data interface
GEMC	Gibbs ensemble Monte Carlo
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
IPE	Institute of Process Engineering, Chinese Academy of Sciences, Beijing
ITO	indium–tin oxide
IUPAC	International Union of Pure and Applied Chemistry
J	coupling constant (NMR)
KWW	Kohlrausch–Williams–Watts
LCEP	lower critical end point
LCST	lower critical separation temperature
LEAF	Laser-Electron Accelerator Facility
LF-EoS	lattice-fluid model equation of state
LLE	liquid–liquid equilibria
LMOG	low molecular weight gelator
LUMO	lowest unoccupied molecular orbital
m	multiplet (NMR)
M	molar concentration
MBI	1-methylbenzimidazole
MCH	methylcyclohexane
MDEA	methyl diethanolamine; bis(2-hydroxyethyl)methylamine
MEA	monoethanolamine; 2-aminoethanol
MFC	minimal fungicidal concentrations
MIC	minimal inhibitory concentrations
MMM	mixed matrix membrane

MNDO	modified neglect of differential overlap
m.pt.	melting point
MSD	mean square displacement
3-MT	3-methylthiophene
MW	molecular weight
MWCNTs	multi-walled carbon nanotubes
m/z	mass-to-charge ratio
NBB	1-butylbenzimidazole
NCA	*N*-carboxyamino acid anhydride
NE equation	Nernst–Einstein equation
NES	New Entrepreneur Scholarship
NFM	*N*-formylmorpholine
NIP	neutral ion pair
NIT	neutral ion triplet
NMP	*N*-methylpyrrolidone
NOE	nuclear Overhauser effect
NRTL	non-random two liquid
NRTL-SAC	non-random two liquid segmented activity coefficients
OKE	optical Kerr effect
p	pressure
PAO	polyalphaolefin
PDMS	polydimethoxysilane
PEDOT	poly(3,4-ethylenedioxythiophene)
PEG	poly(ethyleneglycol)
PEM	polymer–electrolyte membrane
PEN	poly(ethylene-2,6-naphthalene decarboxylate)
PES	polyethersulfone
pH	$-\log_{10}([H^+])$; a measure of the acidity of a solution
PID	proportional integral derivative
pK_b	$-\log_{10}(K_b)$
PPDD	polypyridylpendant poly(amidoamine) dendritic derivative
(PR)-EoS	Peng-Robinson equation of state
PS	polystyrene
PSE	process systems engineering
psi	1 pound per square inch = 6894.75729 Pa
PTC	phase transfer catalyst
PTFE	poly(tetrafluoroethylene)
PTx	pressure–temperature composition
r	bond length
RDC	rotating disc contactor
REACH	Registration, Evaluation, Authorisation and restriction of CHemical

	substances
(RK) EoS	Redlich–Kwong equation of state
RMSD	root mean square deviation
RT	room temperature
s	singlet (NMR)
S	entropy
$scCO_2$	supercritical carbon dioxide
SDS	sodium dodecyl sulphate
SED	Stokes–Einstein–Debye equation
S/F	solvent-to-feed ratio
SILM	supported ionic liquid membrane
SILP	supported ionic liquid phase
SLE	solid liquid equilibrium
SLM	supported liquid membrane
t	triplet (NMR)
TBP	4-(*t*-butyl)pyridine
TCEP	1,2,3-tris(2-cyanoethoxy)propane
TEA	triethylamine
TEGDA	tetra(ethyleneglycol) diacrylate
THF	tetrahydrofuran
TIC	toxic industrial chemical
TMB	trimethylborate
TMP	trimethylpentene
TOF	time-of-flight
UCEP	upper critical end point
UCST	upper critical solution temperature
UHV	ultra-high vacuum
VFT	Vogel−Fulcher−Tammann equations
VLE	vapour–liquid equilibria
VLLE	vapour–liquid–liquid equilibria
VOCs	volatile organic compounds
v/v	volume for volume
w/w	weight for weight
wt%	weight pe rcent
X	molar fraction
γ	surface tension
δ	chemical shift in NMR

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Ionic Liquid and Petrochemistry: A Patent Survey

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Abstract

Industrial applications of ionic liquids in petrochemistry have been reviewed through the US and EP granted patents published from 1990 to 2010. A *Chemical Abstracts* search on the STN host retrieved about 300 patents, about 130 of them found relevant and are fully analysed in this chapter. This survey has been divided into six thematic sections: new formulations and methods of fabrication for an improved use of ionic liquids; separation processes using ionic liquids; use of ionic liquids as additives with specific properties; use of ionic liquids as both acidic catalysts and solvents; applications of ionic liquids as solvents of catalytic systems; and ionic liquids and biopolymers. Our study has been complemented by a short description of the emerging areas concerning ionic liquids using the patent applications published during the past five years.

1.1 Introduction

Interest in ionic liquids has been growing rapidly worldwide, as demonstrated by the increasing number of publications and patents these last years. The applications and the prospects for ionic liquids are vast. In the chemical and petrochemical industries, numerous applications and benefits of using ionic liquids have been described. However, it is difficult to know which applications have been translated into viable industrial and commercialised processes.

As news releases and scientific publications are a part of company strategic communication, relevant information is difficult to assess. We assumed that granted patents could be one of the most relevant sources of information. From our perspective, companies generally only devote human resources, and pay all the necessary fees to have their patents granted, if they expect an actual industrial development of the claimed invention.

A bibliographic search was performed on the *Chemical Abstracts* database using the STN host. It retrieved about 4000 patent families dealing with “ionic liquids.” Among these patent families, about 500 contain a US or EP granted patent during the period from 1990 to 2010. After a keyword restrictive search to the petrochemicals and oil area, we selected about 300 documents. We then fully analysed the most relevant documents, and these are reported in this chapter.

1.2 New Formulations and Methods of Fabrication for an Improved Use of Ionic Liquids

In recent patents, improved ionic liquid formulations and new mode of preparations have been disclosed. Some ionic liquids have been claimed as new products. The aim of these inventions is generally to provide either new cations or new anions or both for ionic liquids with higher purity, such as halogen-free ionic liquids. These formulations are claimed to be advantageous when ionic liquids are used as solvents in catalytic reactions. The most cited reactions are hydroformylation, hydrogenation, and oligomerisation or isomerisation. It appeared to be of interest to review here these new ionic liquids and their preparation processes.

1.2.1 Alkyl Sulfate Ionic Liquids

Several patents devoted to halogen-free ionic liquid synthesis, mainly based on sulfate anions, have been filed by Merck GmbH or Solvent Innovation. In these patents [1], the use of onium alkyl sulfate ($[C_nSO_4]^-$; $n = 3 - 36$) salts is claimed in various processes, including their use as solvents for catalytic reactions, such as hydroformylation, hydrogenation, oligomerisation, and isomerisation. Sulfate ionic liquids are described as being more friendly than halide ionic liquids, which often lead to corrosion and/or disposal issues. In particular, long chain alkyl sulfate ionic liquids are preferably claimed thanks to their improved stability to hydrolysis compared with the methyl sulfate analogues. Examples give a comparative hydrolysis stability study of 1-butyl-3-methylimidazolium methyl sulfate, $[C_4mim][C_1SO_4]$, and 1-butyl-3-methylimidazolium octyl sulfate, $[C_4mim][C_8SO_4]$. At 80 °C, the octyl sulfate is stable for more than 2 hours, whereas methyl sulfate exhibits rapid degradation. These long chain 1,3-dialkylimidazolium alkyl sulfates are prepared through ion exchange process between 1,3-dialkylimidazolium chloride and sodium alkyl sulfate salts.

New imidazolium and pyridinium ionic liquids bearing anions of general formula $[Me(OCH_2CH_2)_nOSO_3]^-$ or $[Me(OCH_2CH_2)_nSO_3]^-$ are also reported [2]. These sulfates and sulfonates are claimed to be more stable to hydrolysis than their methyl sulfate analogues, and to have higher thermal stability. Examples show a comparative hydrolysis stability study of 1-butyl-3-methylimidazoliummethyl sulfate