MATERIALS SCIENCE AND TECHNOLOGIES

PROPERTIES AND APPLICATIONS OF

Noureddine Abidi Julia L. Shamshina



Materials Science and Technologies



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Properties and Applications of Ionic Liquids



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This book is dedicated to my wife Amal, and my kids Merwan and Nabil, and in memory of my late father, mother, and sister. You are always with me.

Noureddine Abidi, Ph.D.

To my late father, Leonid Fyodorov.

J. L. Shamshina, Ph.D.

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Preface

This book reviews recent developments in the field of ionic liquid (IL). The ILs are composed of ions chosen to achieve maximum destabilization of the crystalline solid state of the substance. In Walden's original paper (1914) which examined the electrical conductivity and the molecular size, of mono-, di- and tri-alkylammonium nitrates, he described this class of substances as "salts that exist in a liquid state under standard conditions due to the peculiarities of their chemical structure", and mentioned that "the behavior of these organic salts at temperatures below or around 100°C resembles experiences with inorganic molten salts".

There are many ions that might be selected for the IL formation using "anti-crystal engineering" approach, by balancing of ions symmetry and interionic interactions. ILs are structurally organized on different length scales, from supramolecular (ion clusters) to mesoscopic (hydrogen-bonding networks). Using appropriate combinations of the component ions, it is possible to prepare ILs with essentially any structure and targeted physicochemical properties. The presence of ions results in a number of unique properties, such as wide liquid ranges, non-volatility, and high decomposition temperatures. However, there are many claims accepted as true by the members of the wider scientific communities, – ILs are green, ILs do not burn, ILs are non-toxic, – that eventually were found to be speculative due to limited scientific findings available at the time, and erroneous impressions about the degree of certainty. The overview of ILs is covered in Chapters 1 and 2.

The field has gained a substantial growth from 1990 onwards, due to efforts by the United States Air Force (AFOSR) in applying ILs as electrolytes. Indeed, ILs with high electrical conductivity, high dielectric constants, large electrochemical windows, and redox-stability have been utilized in a number of electrochemical processes, in batteries, capacitors, photovoltaic devices, and electrochemical sensors. Electrical conductivity and dielectric properties of ILs and their solutions are discussed in Chapter 3.

Researchers have been able to knowledgeably prepare ILs based on desired properties for specified purposes, by selecting the ions that are able to impart needed characteristics, at the same time maintaining the core desirable features of the liquid state of matter. Investigations of the various ions and their combinations at the molecular level provided the understanding for the rational development of tailored ILs, so-called Task Specific Ionic Liquids (TSILs), in which a functional group is covalently attached to one (or both ions), for a specific task. This included TSILs for the replacement of volatile amines in reversible capture of CO₂, covered in Chapter 4. The book also covers another type of TSILs, surface-active ILs ("SAILs"), that possess both polar hydrophilic and hydrophobic group in their structure, whose properties and applications are covered in Chapter 5. While initially SAILs found applications in synthesis and catalysis, their usage was later expanded to other areas, such as petroleum industry (covered in Chapter 6).

Another important application of ILs is their extensive utilization in pharmacology, biomedicine, and, lately, biotechnology. Historically, ILs been used as active pharmaceutical ingredients (API-ILs) and as solvents in pharmaceutical industry, for the synthesis of drugs or drug intermediates, pharmaceutical crystallization, continuous manufacturing, and drug delivery of poorly water-soluble drugs. Since recently, they have been employed as relevant alternative solvents to conventional media for stabilization, processing, handling, and storage of nucleic acids. This relatively recent area of investigations is covered in Chapter 7.

Perhaps, the most important application of ILs is their utilization as new solvent systems with enhanced, or even unique, performance. This included IL-assisted graphite exfoliation, the method that has high potential to improve commercial availability of graphene. In this process, the cation–anion coordination, particularly π -stacking in the case of aromatic cations, contributed significantly to the success of the exfoliation process (Chapter 8). ILs provide suitable replacements for volatile organic compounds (VOCs) identified as significant environmental pollutants thus being extensively used for a wide range of separations. Heavy metal ions extraction is covered in Chapter 9, whereas separation of pollutants is covered in Chapter 10.

Importantly, ILs are suitable for the pre-treatment of various biomasses such as wood (hardwood and softwood), grasses, crop residues, and agricultural biproducts (e.g., crustacean biomass). There are numerous IL-based technologies now available for the separation of biopolymers from biomasses which offer the opportunity to use the clean separated biomass components as a reproducible feedstock for further valorization into chemical building blocks, or for the preparation of advanced materials from them. Experimental insight into cellulose dissolution mechanism in ILs/cosolvent mixed systems is covered in Chapter 11. These unique solvent properties of the ILs opened up scope for new applications and improvements in existing technologies. Thus, a process called "natural fiber welding" allows for transformation of loose cellulosic (or protein) fibers into congealed network using an IL solvent, to increase the performance of biopolymer-based (cotton, silk) textiles. The state of natural fiber welding technology is covered in Chapter 12. In summary, the book strongly indicates the significant activity currently taking place in the IL field, and the future holds many new discoveries.

Chapter 1

What Are Ionic Liquids? Embracing the Immensity

Paula Berton¹ Noureddine Abidi² and Julia L. Shamshina²

 ¹ Chemical and Petroleum Engineering Department, University of Calgary, Calgary, Alberta, Canada
² Fiber and Biopolymer Research Institute, Department of Plant and Soil Science, Texas Tech University, Lubbock, Texas, USA

Abstract

Considering the rapid development of this class of compounds and exponential growth in applications, summarizing what ionic liquids (ILs) are is "embracing the immensity". The perception of ILs has changed and keeps changing, or rather evolving, over time. It is a dynamic, ongoing process with a capacity for self-correction, like any scientific learning. The needs of users of ILs change, and new technologies and new products require new and efficient systems.

Keywords: ionic liquids, ionicity, applications of ionic liquids, ionic liquid processes, ionic liquid types

Introduction

A brief and, at the same time, up-to-date and original introduction is a challenge when it comes to summarizing the ionic liquid's (ILs) field progress, even when the active development of the field of ILs has taken place for only the last four decades. One could think that trying to condense what ILs are in a few pages feels like "embracing the immensity," considering the rapid development of this class of compounds and exponential growth in applications.

Out of the numerous reviews available on the topic, three stand out, since they are written by some of the founders of the field – John Wilkes (2002) [1], Austen Angell (2012) [2], and Tom Welton (2018) [3]. While citations of the original research papers are typically preferred over citations of review articles, these works highlight the early chronicles of the field and are

In: Properties and Applications of Ionic Liquids Editors: Noureddine Abidi and Julia L. Shamshina ISBN: 979-8-88697-635-9 © 2023 Nova Science Publishers, Inc. well spread out in time, allowing interested readers to closely follow the development of the discipline. There is also an interesting perspective that looks at the ILs through the lens of patenting field [4]. This work reviewed patents and claims and provided an overview of IL-based technologies from the point of their commercial potential, elucidating trends toward new applications for ILs. Finally, a recent book chapter by Roland Kalb on the industrialization of ILs summarized the opinions of academic and industrial leaders in the field and gave an overview of both pilot and fully commercialized IL-based technologies [5]. It also identified opportunities and future research areas.

The field as we know it originated from catalytic and electrochemical studies conducted using room-temperature molten salts - substituted alkylpyridinium and imidazolium chloroaluminates [6-12]. It was Professor Ken Seddon, who, when became fascinated with these "neoteric solvents", co-founded the Queen's University Ionic Liquids Laboratory Research Centre (QUILL) [3]. This was the first research center that partnered with industrial companies: BP Chemicals, Shell, Proctor and Gamble, Petronas, Unilever, Imperial Chemical Industries (ICI), etc., to work on ILs for the research on clean technologies and catalysis [13]. In 2000, Ken Seddon, Robin Rogers, and Sergey Volkov organized a NATO Advanced Research Workshop "Green Industrial Applications of Ionic Liquids", the first international meeting dedicated to the area of ILs [14], which laid the foundation for a new era in using ILs for green technologies. Soon after that, multiple conferences and symposia dedicated to ILs followed, including the 1st International Congress on Ionic Liquids (COIL) in Salzburg, in 2005. Now, the list of conferences on ILs is exhaustively long and includes the Ionic Liquid Conference, Ionic Liquids in Chemical and Biochemical Systems Conference, Ionic Liquids in Purification Technologies Conference, Ionic Liquids in Separation and Purification Technologies Conference, Chemistry of Ionic Liquids Conference, Gordon Research Conference on Ionic Liquids, not to mention numerous IL symposia [15].

"All Our Knowledge Has Its Origins in Our Perceptions" (Leonardo Da Vinci)

The perception of ILs has changed and keeps changing, or rather evolving, over time. First of all, it is a dynamic, ongoing process with a capacity for self-correction, like any scientific learning. Secondly, the needs of users of ILs change, and new technologies and new products require new and efficient systems. Historically, ILs were defined as ionic compounds with a melting point below the boiling point of water (100°C), and multiple research articles claimed it was Tom Welton who introduced this temperature limitation in his 1999 review [16]. According to Tom Welton himself, this was most certainly not the case [3]. Instead, he recommended that the term "ionic liquid" assumes low-melting salt. Yet, as Isiah Warner put it when talking about GUMBOS (Group-of-Uniform-Materials-Based-on-Organic-Salts): "There is no logical reason why we cannot extend our melting point range to 250°C while maintaining the tunability which is inherent to ILs" [17]. Nonetheless, right now the term IL assumes an ionic compound with a melting point below 100°C, often below room temperature (room-temperature ILs or RTILs).

It was also initially declared that "ILs are composed solely of ions" [18, 19]. The question of this restrictive nomenclature is looked at as a limitation in the field after the development of

multicomponent systems of intermediate ionicity [20]. In 2010, the term "confused" or oligomeric ILs was introduced, where ILs contained oligomeric hydrogen-bonded cations or anions [21]. Investigations at the molecular level revealed that a large number of liquid forms exhibited what was called "intermediate ionicity". These are hydrogen-bonded complexes [19,22] of ionized and unionized forms that share a delocalized proton [20]. In simplified terms, these systems are somewhere in between fully ionized (i.e., ILs) and non-ionized (i.e., deep eutectic solvents) structures [23-26]. As an example, a simple, protic IL triethylammonium acetate is classified as a complex system with oligomeric ions [27]. This said, we agree that the term "ionic liquids" for this type of liquid salt is somewhat controversial.

That is not to mention that ILs were defined to be composed of an "organic cation and either an organic or inorganic anion". However, systems containing more than two ions, so-called "double salt ionic liquids" (DSILs [28-30]), can be prepared by simply mixing two (or more) ILs. Such mixing allowed manipulating physicochemical properties of the systems through the additional degree of freedom, and often exhibited nonlinear changes in comparison with "original" ILs [31], due to differences in ion interaction energies and formation of hydrogen bonds.

Despite all the controversies about the definition and number of compounds that should be included under the term "ionic liquids", they are game changers: They can be prepared with specific physicochemical properties targeted for a specific process. A sign of their importance and potential is signed by the fact that ILs won the Great British Innovation Vote in 2013 [32] as the innovation presumably able "to shape the 21st century."

A Boom in Applications

It became evident by 2000, that the low vapor pressure of these liquids allows using them as safe solvents [33] for transition metal-catalyzed reactions [34-37], enzymatically-catalyzed reactions [38], and other chemical transformations [39]. Concurrently, Jim Davis introduced the term Task-Specific Ionic Liquids (TSILs), in which a functional group was covalently attached to one or both of the ions of an otherwise "ordinary" IL [40,41], with a particular application in mind: as catalysts [42], chiral solvents [43], magnetically susceptible materials [44], for CO₂-capture [45], and so on (the list of TSILs' is endless!).

The discovery that ILs are suitable for the dissolution of biopolymers and biomasses [46] opened a whole new avenue of research. Initially, biopolymer-dissolving halide-containing ILs were used for the purpose [47,48]. This was followed by the current state-of-the-art acetate-based ILs [49,50], produced according to the patented CBILS[®] halide-free process. Later on, super-base ILs with high dissolution power were developed [51,52]. Out of the relatively recent processes, it is worth mentioning the HighPerCellCarbon[®] process which involves the wet-jet spinning of cellulose fibers from ILs followed by transformation into carbon fibers by carbonization [53,54].

Around 2007, the study of ILs in the pharmaceutical industry was initiated [55]. Initially, ILs were used as solvents in the synthesis of drugs or drug intermediates, solvents for extraction of drugs from natural products, and as solvents, co-solvents, anti-solvents and emulsifiers in pharmaceutical separations and continuous pharma manufacturing. As the field developed, ILs were used as pharmaceutical ingredients, as a tool to reformulate APIs into more bioavailable forms [56,57] where liquefaction was a result of "anti-crystal engineering" [58] or combining

an IL strategy with the prodrug strategy to improve the delivery of solid APIs, representing an enabling technology platform. Even though the concept of API-ILs provides integrated drug design, development, and manufacturing, and the numerous academic studies, there are limited examples of commercialization, such as the case of a reverse transcriptase inhibitor for the treatment of HIV from GlaxoSmithKline (GSK), GSK2838232 [59-61] or CAGE [62].

Conclusion

In these transitioning times, when the world is looking for alternative, more sustainable technologies, ionic liquids can, once again, be part of innovative, revolutionary solutions, for example, in battery-related and energy storage applications [63-67], to solve obstacles in solar cells-based photovoltaics technology [68,69] and to reduce the human impact on the environment by capturing CO_2 or toxic gases such as mercury from gaseous effluents [70-76] or by treating industry-generated tailings [77], to name a few.

The list of applications and innovations unlocked by ILs goes on and on, and some of the latest advances are already turning into processes and innovations to answer real-world problems in different fields [78]. Nowadays, it is not uncommon to read in the news about scaling up IL-based technologies. For example, Ioniqa Technologies is a Dutch polyethylene terephthalate (PET) recycler that uses ILs to convert colored PET waste into a monomer for producing new PET [79]. Ioniqa's demonstration plant can digest 10,000 tonnes of PET annually, and Koch Industries recently announced a \$30 million investment to help scale up the process [80]. Although many of these technologies are well-developed and de-risked, technological innovations based on ILs continue to emerge each year, and ILs are still demonstrating that their tunability can be used in the large domain of cutting-edge fields. For example, the tunable properties of ILs were recently used, for the first time, in physical reservoir computing (PRS) systems, allowing a versatility that was unthinkable before. This new IL-based PRS design could lead to Artificial Intelligence devices that can directly learn at the time scales of environmentally generated signals, in real-time [81].

This book presents recent trends in different areas of ILs chemistry and technologies. The readers will find eleven chapters on recent applications of ILs in the fields of the petroleum industry, stabilization of nucleic acids, separations, and biopolymers' processing, including trends and critical perspectives.

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Chapter 2

Ionic Liquids: From Laboratory Research to Industrial Applications

George G. Tamas*

Bradley University, Peoria, Illinois, USA

Abstract

Since their discovery at the beginning of the 20th century, ionic liquids have gained much attention in the academic and industrial worlds. Their structure, based on a virtually unlimited combination of cations and anions, is responsible for their high tunability. As organic salts – with remarkable properties such as wide liquid range at relatively low temperatures, negligible vapor pressure, good thermal stability, and broad electrochemical windows – ionic liquids have exceptional solvation properties adjustable to target a wide range of applications, including, but not limited to, chemical catalysis, textiles, energy storage, sustainable lubricants, energy storage, bioactive compound extraction, membrane separation, and pharmaceuticals. Although the research on ionic liquids grew rapidly starting in the early 1990's, the technological transfer from the laboratory to industrial applications has not been as fast paced. This chapter summarizes some remarkable scientific breakthroughs that proved to be successful industrial transitions.

Keywords: ionic liquids, industry, commercial applications

Introduction

In 1914, Paul Walden published his research on ethylammonium nitrate ($[EtNH_3][NO_3]$) and reported some unique physical properties of the new chemical formed by the neutralization of ethylamine with concentrated nitric acid [1]. This compound had an unexpected feature; its melting point was below room temperature, at around 12°C. Other salts become liquids only at much higher temperatures (e.g., NaCl m.p. = 801°C, CaCl₂ m.p. = 772°C) [2]. Although Walden's paper did not reach a large audience at the time, a century later, his work is considered the starting point of a new dynamic chapter of chemistry: ionic liquids.

^{*} Corresponding Author's Email: gtamas@fsmail.bradley.edu.

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The name ionic liquids (ILs) acknowledges the uniqueness of these molten organic salts. Those in liquid state below 25°C are called room-temperature ionic liquids (RTIL). A more flexible definition of ILs comprises all the organic salts with melting points under 100°C [3]. Ionic liquids are built of organic cations and organic or inorganic anions, and the type of ions combined dictate their properties that makes the ILs highly tunable chemicals, which is why some scholars consider them *designer solvents*.

Several comprehensive reviews on ILs properties, synthetic protocols, purification methods, and fields of applicability have been published [4, 5, 6, 7, 8, 9, 10]. The ILs field has had a fast-paced growth with the start of the 21st century, becoming a fully mature and stable area of research, with over eight thousand papers published yearly for the past decade (Figure 1).





In the ILs field, commercial fruition of the new technologies has been delayed, with an apparent disconnection between the research publications trend and the investment in production facilities. It has been argued that the ILs field followed a hype curve where the peak of high technological expectancy was followed by a trough of disillusionment. However, the current status continues on a steady growth [11].

This chapter summarizes the IL-based technologies that are already well established commercial applications as well as the ones at the start-up stage and it is structured according to the role of the ILs in the fields of application: solvents and catalysis, electrochemistry, functional fluids, and analytical chemistry.

Solvents and Catalysis

Ionic Liquids and Cellulose Dissolution

Cellulose is a ubiquitous biopolymer provided by nature at a billion tons scale [12, 13]. As the main structural constituent of plants, cellulose is a regenerable resource with numerous

potential applications. Still, its lack of solubility in water or other common solvents was for a while the main impediment in its processability [14]. Solutions to this problem were proposed and two procedures were well established and scaled up, viscose [15] and lyocell [16]. Viscose fibers (also known as rayon) are obtained mainly from wood pulp, after the cellulose is chemically modified by treatment with sodium hydroxide, followed by derivatization with carbon disulfide. Then dopes with low viscosity undergo wet spinning through a spinneret immersed in an aqueous bath of sulfuric acid. This procedure has a heavy environmental load since carbon disulfide is toxic and it is not fully recovered [17]. Conversely, lyocell fibers are produced through a direct dissolution technique rather than a chemical protocol and benignly replaces hazardous compounds such as carbon disulfide with the less harmful N-methyl morpholine-N-oxide (NMMO) [18]. Unfortunately, NMMO is a thermally labile compound and, as an oxidant, is sensitive to catalytic impurities, requiring the addition of stabilizers to the dope at an early stage of dissolution [19]. This procedure is environmentally friendly, with more than 99% of solvent recovery per production cycle, although it still involves a significant amount of energy in solvent recycling [20].

As early as 1934, Graenacher patented N-alkylpyridinium organic salts as direct solvents for cellulose, both pure and mixed with suitable diluents [21]. However, it took more than half a century until Swatloski discovered that 1-butyl-3-methylimidazolium chloride IL could dissolve cellulose without activation or pretreatment, triggering an increase of research on this subject [22, 23].

Based on these findings, two novel approaches have been successfully developed and are currently going through the early start-up commercial stages. In the United States, Natural Fiber Welding Inc. patented the *fiber welding* technology, which employs 1-ethyl-3-methylimidzolium acetate [EMIm][OAc] IL and a molecular solvent to transform cellulose into a *congealed network* while still conserving the native biopolymer structure [24]. The raw cellulose fibers are briefly exposed to the appropriate formulation of the *welding solvent* without allowing a complete dissolution. The outer fibrous layer is swollen and solubilized by the IL, disrupting the hydrogen bonding network. The gained mobility of the cellulose permits interaction with the surfaces of the contact fibers and consequently the reshape of the material. Reaction quenching by adding an antisolvent and removing the IL generates a yarn with a completely new morphology (Figure 2) [25]. The new morphology (Figure 3) generates fabric with improved durability, abrasion resistance, reduced pilling and moisture management properties [25]. Furthermore, it allows the upcycling of shorter fiber yarns which are usually considered not desirable by the textile industry [26].

The second approach in development occurs in Finland, where researchers from Aalto University and the University of Helsinki developed Ioncell[®] [27], a dry-jet wet spinning technology, employing 1,5-diazabicyclo[4.3.0]non-5-ene acetate [DBNH][OAc] as cellulose dissolution agent (Figure 4a) [28].

Similar to the welding protocol, the acetate anion disrupts the hydrogen bonding network, but in this case, a full dissolution of the cellulosic wood pulp occurs at moderate temperatures. Once the homogenous, viscous, dope is formed, a piston extruder is used to spin it, via a multihole spinneret. Continuous filaments are generated, subsequently exposed to an air gap, and then coagulated in a cold water bath (Figure 4b) [29, 30]. Highly oriented cellulose fibers are produced with tenacities consistently above 50 cN/tex and high initial moduli of up to 34 GPa [29].

Figure 2. Representation of the welding protocol. It starts with two separate cellulosic yarns (A) that are briefly exposed to the IL-organic solvent formulation promoting the rearrangement of the outer shell fibers (B), leading to the reconstituted single yarn post-reaction quenching (C). At the polymer level, the strong H-bonding network (D) is disrupted by the insertion of the ionic liquid ions (E), which subsequently are removed (F). Reprinted with permission from ref [25] Copyright ©2021 American Chemical Society.

Raw Yarn



Figure 3. SEM cross (left column) and longitudinal (right column) sections of a cotton yarn. The upper row depicts a raw yarn, whereas the lower row shows the same material after applying the welding treatment – *welded yarn*. Reprinted with permission from ref [25] Copyright ©2021 American Chemical Society.





Figure 4. a) Structure of [DBNH][OAc]; b) Schematic of Ioncell® dry-jet wet spinning process.

While showing remarkable cellulose dissolution capabilities, both IL-based techniques have to overcome two major disadvantages: the cost of ILs (not a commodity chemical yet) and the need to quantitatively remove the water from the operating fluids. Water removal could be achieved by developing a highly efficient solvent recycling system, although it comes with the adjacent capital expense.

Biphasic Acid Scavenging Utilizing Ionic Liquids (BASIL)

One of the first multi-ton scale commercial application involving ILs was introduced in 2002 by BASF under the trade name BASILTM (i.e., Biphasic Acid Scavenging utilizing Ionic Liquids) at its production plant in Ludwigshafen, Germany. This new procedure improved the synthesis of alkoxyphenylphosphines, precursors of Lucerine® photoinitiators used in UV curing of coatings and printing inks [31–34]. The original chemical protocol generated hydrochloric acid as by-product that was trapped with trietilamine (Figure 5). The tertiary ammonium chloride formed separates as a solid non-stirrable paste, which becomes relatively difficult to manage in large scale production [32].



Figure 5. The original synthesis of the alkoxyphenylphosphines using tertiary amines as acid scavengers.

By replacing the triethylamine base with 1-methylimidazole, an IL is generated: 1methylimidazolium chloride ([HMIm][Cl]) (Figure 6). Since the organic salt is liquid at the reaction temperature, a clear biphasic system is formed, allowing a facile separation of the phosphine derivative target molecule and decreasing the volume of the reactor [35]. Also, because 1-methylimidazole acts as nucleophilic catalyst, the reaction time is decreased to under one second and the productivity of the process is increased by a factor of 104 [36].



Figure 6. BASF's BASIL protocol for the generation of the IL 1-methylimidazolium chloride ([HMIm][Cl]).

Replacing Toxic Phosgene with Nucleophilic HCI

The toxicity of various chlorinating agents such as phosgene or thionyl chloride is well known, and it is a real hazard when the processes occur at an industrial scale [37]. The chlorination of aromatic alcohols in the presence of hydrogen chloride was reported by Earle in 2004 [38]. However, attempts to chlorinate 1,4-butanediol (BDO) in similar conditions generated large amounts of secondary products (i.e., tetrahydrofuran (THF), 4-chloro-1-butanol (CBO)) and only a small quantity of the target product: 1,4-dichlorobutane (DCB) (Figure 7a) [39]. A new alcohol chlorination protocol (patented by BASF, 2005) solved this problem by replacing the toxic phosgene with *nucleophilic HCl* as a halogenating agent in the presence of ILs. Under the activating effect of the organic salt, more than 98% selectivity towards DCB product was achieved (Figure 7b) [40].



Figure 7. Reaction of BDO with nucleophilic HCl. Product amount distribution a) in absence of the ionic liquid; b) in presence of the ionic liquid.

DIFASOLTM Dimerization

In the oil refining industry, the fluid and steam cracking processes are a significant source of light olefins (C2-C5 fractions). Oligomerization of these olefines by homogenous catalysis adds value to lower grade chemicals. In 1977, the Institut Français du Pétrole (IFP) developed and

Ionic Liquids

commercialized an alkene dimerization protocol under the trade name Dimersol [41, 42] (Figure 8). The catalytic system involved in the process was based on a cationic complex that generates an activated nickel hydride species (Ni-H)+ [41]. Homogenous organometallic catalysis, under right metal-ligand and metal-activator selections, provides better control of the final product. Depending on the feed, Dimersol GTM and Dimersol XTM were licensed out for dimerization of propene and butenes into more desirable hexenes and octenes [43].



Figure 8. Dimerization of a terminal alkene generating a mixture of isomers (dashed lines representing the points of variability).

Specifically, a soluble nickel (II) metal and a chloroaluminium derivative co-catalyst (i.e., $Ni(II) + AlCl_{3-x} Et_x$) generate *in situ* the active species used in the nonregioselective industrial dimerization of low cut alkenes (C2-C4), with an observed decreasing olefine reactivity going from ethylene to n-butenes [44, 45]. Unfortunately, the catalyst recyclability requires a water wash step that has negative effects on the overall yields and production costs [46].



Figure 9. DIFASOL dimerization. Reprinted with permission from ref [41]. Copyright ©2021 American Chemical Society.

To surpass the DimersolTM monophasic protocol limitations, IFP further developed DifasolTM, as an IL-based biphasic system [44, 47]. The technique exploits the immiscibility of the dimerization product into the IL-catalyst phase, where the reaction takes place. This

difference in miscibility enables a facile separation by simple phase decantation. A decrease in the Ni(II) catalyst consumption and better dimer selectivity were reported [47]. Also, since both phases are liquids, there is an improved mixing and heat transfer, with a direct effect on the volume of the reaction vessel. Furthermore, the new approach handles more efficiently the diluted monomer feedstocks [43]. The Difasol process can be retrofitted to the current Dimersol production units reducing the capital expense (see Figure 9).

ISOALKY: Ionic Liquid Alkylation Technology

The negative environmental impact of the fuel burnt in the internal combustion engines is a cause of great concern worldwide, resulting in an oil industry heavily regulated [48]. Consequently, refiners and fuel blenders have to meet rigorous air quality standards while still delivering cost-efficient fuels. To develop cleaner-burning gasoline, several approaches have been explored, including the IL alkylation technology.

Alkylate is a mixture of C7 and C8 naphtha-range hydrocarbons resulting from the isobutane's reaction with light olefins [49]. Alkylate gasoline is characterized by a high octane number, low sulfur content, zero aromatics, and reduced fuel volatility and evaporative emission (Reid vapor pressure) [50]. According to the American Fuel and Petrochemical Manufacturers association, alkylate gasoline is essential in complying with a series of recent regulations such as California demand for reformulated gasoline, Clean Air Act Reid Vapor Pressure-compliant fuel, and the Corporate Average Fuel Economy targets for mileage efficiency and carbon reduction [48].

The traditional alkylation technologies employ either hydrofluoric or sulfuric acid catalysts to produce alkylated gasoline, with a relatively equal distribution of the two chemical routes among the existing refining plants in the US [51]. The reaction is based on acid-promoted generation of carbocations provided by the C3-C5 Fluid catalytic cracking (FCC) olefins, which react with the isobutane in a subsequent step (Figure 10). Unfortunately, both acid catalysts have a heavy environmental footprint and raise safety manipulation concerns.





Chevron (United States) and Honeywell UOP (United States) developed ISOALKY technology for the production of alkylate gasoline using non-volatile and environmentally friendly ILs [52, 53]. Specifically, ISOALKY protocol uses a chloroaluminate IL catalyst and employs anhydrous hydrochloric acid as co-catalyst [50].

The superacid properties of the chloroaluminate organic salts were previously investigated by Ma and collaborators. A 2:1 ratio of aluminum chloride: trimethylsulfonium chloride (TMSuCl) in the presence of 1 atm hydrochloric acid formed several aryl and arylalkyl carbocations that could be analyzed by NMR and UV-Vis spectroscopy (Figure 11). The protonation of the liquid hydrocarbons takes a couple of minutes, whereas the protonation of the solid compounds can take around 15 min [54].



Figure 11. Various carbocations produced by superacid chloroaluminate organic salts in the presence of HX ($R_1 = Me, R_2 = Ph, Me, H$).

The ISOALKY system is described as an "anhydrous AlCl₃ - based Lewis acid catalyst promoted with anhydrous hydrochloric acid, Brønsted acid and exhibiting the characteristics of a superacid." This strong acidity has an immediate beneficial impact on the size of the reactor and the amount of catalyst needed in the total reaction mass to promote alkylation, which is decreased from over 50% in the case of conventional HF/H₂SO₄ to 3-6% for the new IL approach [50].

The organic salts claimed in the Chevron ISOALKY patents are hydrocarbyl substituted pyridinium or imidazolium chloroaluminate compounds (Figure 12), where the anion is $Al_2Cl_7(-)$. All of them are liquid salts and, as catalysts, show the highest Lewis acidity when the mole fraction of $AlCl_3$ in the IL is $x(AlCl_3) = 0.67$ [50]. The new procedure can alkylate feedstocks spanning from ethylene to amylenes, while using only trace amounts of hydrochloric acid co-catalyst recycled *in situ* [55].



Figure 12. Structures of the ILs present in the ISOALKY catalyst.

Chevron completed commissioning the first commercial IL–based alkylation unit at its Salt Lake City refinery in 2021. Honeywell UOP announced that Big West Oil (United States) and Tüpraş (Turkey) refineries will revamp their hydrofluoric acid units to the ISOALKY technology [56, 57].

SILP Catalysis

The Supported Ionic Liquid Phase (SILP) catalysis refers to a methodology of converting a purely homogeneous catalyst system into a heterogeneous one [58, 59, 60, 61]. A SILP catalyst structure has three key components: a solid supporting material, an IL, and the active catalyst (Figure 13).



Figure 13. A SILP catalyst is a heterogeneous system providing a homogeneous IL-catalyst layer where the starting material (SM) is converted into product (P).

Traditionally, the solid support material is an inert porous substrate with a large internal surface area that fulfills only a mechanical role. This surface is subsequently coated with a homogeneous mixture of an IL and the catalyst. The IL is a non-reactive carrier, ensuring a high dispersion of the contained molecular species [62]. Although, the SILP catalyst is in the form of solid pellets or powder, at a microscopic level, the chemistry happens in homogeneous phase, allowing for high selectivity and mild reaction conditions. This setup is especially beneficial for industrially scaled-up processes where an easy separation from the reaction mixtures is always desirable [63].

Natural gas reservoirs are usually contaminated with elemental and oxidized forms of mercury in concentrations ranging from $0.1 - 5000 \ \mu g \ m^{-3}$ [64]. All these forms of mercury (i.e., Hg(0), Hg(I), and Hg(II)) are known to be toxic [65] and corrosive, impacting the personnel and causing irreversible damages to the aluminum-based equipment via a liquid-metal-embrittlement mechanism [66].

Petronas (Malaysia), in collaboration with Clariant (Switzerland) and the scientists at Queen's University Ionic Liquids Laboratory (QUILL, United Kingdom), developed a scrubbing agent for the extraction of elemental, organic, and inorganic mercury from natural gas [67]. Abai and collaborators' initial work with [C4mim]Cl-CuCl2 and [N₄₄₄₁]Cl-CuCl₂ couples, at a χ CuCl₂ = 0.50 ratio, supported a reaction with mercury following the mechanism described by Eq. (1):

$$2[Cu_2Cl_6]_2^- + 2Hg(0) \to [Hg_2Cl_6]_2^- + 2[CuCl_2]^- + 2CuCl(s)$$
(1)

The equation suggests that a liquid phase IL-based mercury scrubbing from natural gas is possible. Still, a scale-up would be less sustainable at the industrial level, considering the viscosity of the organic salts. Employing the SILP methodology, QUILL researchers proved that mercury vapors from a natural gas effluent could be efficiently trapped in the presence of chlorocuprate(II) ILs impregnated on highly porous solid supports [64]. The heterogeneous approach avoids the slow mass transfer generated by IL's high viscosity while using more efficiently only thin films of IL deposited on the scrubber pellets [62].

In 2014, Clariant and Petronas introduced the results of this research to the market under the trade name HycaPure[™] Hg technology, which claimed to have a lifetime three times longer than sulfur-impregnated activated carbon [67]. Practically, thirty-five years after De Munck and Hjortkjaer (1981) introduced the heterogenization concept of supported liquid phase (SLP) systems, Malaysian oil and gas company Petronas made the mercury removal methodology a fully commercial application [68, 69, 70].

Ionic Liquid Cooling Technology (ILTEC)

Considering the high temperatures required by the various metallurgical processes, the need to cool the aggregates is permanently present and currently fulfilled by water. As a conventional coolant, water has high thermal conductivity and is an available low-cost resource. However, if leaking occurs, and water enters in contact with molten metal, catastrophic explosions may occur. Such event is mainly caused by the rapid volume expansion along with hydrogen gas generation. Therefore, as a precautionary measure, the water cooling systems are restricted to an operating temperature of maximum 60°C and are positioned at higher levels than the metal melt baths [11].

To improve the safety of the personnel and the equipment in metallurgical plants, Mettop GmbH (Austria) and Proionic (Austria) developed ILTEC technology, as an IL-based cooling alternative of the metallurgical equipment involved in producing non-ferrous metals, ferroalloys, and steel [71, 72]. The new working fluid (i.e., IL-B2001) is based on 1-ethyl-3-methylimidazolium tetrafluoroborate (97%) and 1-ethyl-3-methylimidazoliumfluoride (1.5%) organic salts. This non-water cooling medium has several advantages [71, 73]:

- It has excellent long-term stability at operating temperature between 50-200°C, and a short-term stability up to 250°C. This extended working range makes the recovery of the dissipated heat more efficient.
- In case of leaking, IL-B2001 decomposes into elements without a rapid volume expansion or hydrogen gas generation, therefore mitigating the risk of explosion.
- It is produced under a chlorine-free technology, thus it is non-corrosive for the equipment.
- It undergoes crystallization under -30°C, preventing piping damage by freezing volume expansion in case of system failure.

These factors support the transition from a water-cooling operating system placed in a red safety zone to a more desirable green area of operational awareness (Figure 14).

The ILTEC technology could also be retrofitted to the existing water cooling setup since it can remove a comparable amount of heat through the piping and pumping system already in place [71].

Construction-wise, the equipment has three major components (Figure 15):

- A storage tank where IL-B2001 is kept under nitrogen to prevent moisture absorption due to organic salts hygroscopicity.
- A dual redundant pumping system to move the coolant through the piping lines.
- Two heat exchangers for heat release to a secondary cooling circuit.

Mettop's novel technology is already in operation at ArcelorMittal, Luxembourg (2015 – tap hole cooling); Nyrstar, Belgium (2015 – side wall cooling); and Voestalpine Stahl Donawitz, Austria (2017 – flange cooling) production facilities [71].



Consequences

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Figure 14. Consequences vs. likelihood of an incident event, comparing the water-cooling operating system and the IL-based cooling operating system.



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Figure 15. Basic design of an ILTEC equipment.

Electrochemistry

Due to their large electrochemical windows, high ionic conductivities, good thermal stabilities, non-flammability, and non-volatility features, ILs are excellent candidates for the development of electrochemical applications [74]. The two areas of progress where ILs electrolytes showed promising results are metal electroplating and energy storage.

Chromium Electroplating Process

Scionix (Netherlands) developed and patented an IL-analog system designed for chromium electroplating, which can deposit crack-free coatings on metals at more than 90% current efficiency. This is remarkable considering that the traditional aqueous acid-based protocols use only 20% of the overall energy consumed for actual chromium electrodeposition, negatively impacting the economic efficiency of the process [75, 76].

Scionix's formulation is a 1:2 mixture of choline chloride and chromium(III) chloride hexahydrate forming a deep eutectic solvent under the appearance of a dark green viscous liquid at room temperature [77]. Notably, this electrochemical pair eliminates the highly toxic chromium(VI) from its composition. Furthermore, the absence of bulk water reduces hydrogen evolution during electrochemical process and concomitantly mitigates the embrittlement of the coating layer [77].

Energy Storage

Almost fifty years ago, after Oseteryoung and collaborators published a comprehensive study on 1-butylpyridinium chloride and aluminum chloride [78], Nardy, with the United States Air Force support, patented the use of aluminum chloride and the more generic 1-Alkyl pyridinium chlorides room-temperature ILs mixtures as electrolytes for primary and secondary batteries [79]. However, these systems had a high moisture sensitivity problem, where even traces of water would decompose the ILs [80]. Chemical stability issues, along with the ILs' known hygroscopicity, were later largely overcome with the introduction of hydrophobic anions. Specifically, Grätzel synthesized a multitude of hydrophobic imidazolium IL-based on anions such as [OTf]⁻ (trifluoromethanesulfonate) and [NTf₂]⁻ (bis((trifluoromethyl)sulfonyl)amide) [81]. These new room-temperature liquid salts showed much larger electrochemical windows (5-6 V) than water (1.23 V) [82]. Once reliable electrolytes were available, their applicability to energy storage devices such as batteries and supercapacitors was the expected progression.

Lithium-ion batteries are ubiquitous in all lightweight mobile devices. Although their specific energy density is high, an improvement in terms of power density is always desirable [83]. Better electrolytes are an essential channel for lithium-ion batteries advancement. IoLiTec (Germany) offers a suite of battery dedicated electrolytes based on [NTf2]⁻ and [BF4]⁻ anions. They are, in general, combined with relatively small size cations to reduce ILs viscosity and promote good ion mobility [84]. NOHMs Technologies (United States) offers NanoLyte battery electrolytes based on phosphate ILs. The company claims a non-flammable and non-volatile

product with a liquid temperature ranging from -80 to 300°C and good lithium-ion conductivity [85].

Supercapacitors are operationally safe and have a very long lifespan, usually higher by one to two orders of magnitude than lithium-ion batteries [83]. They can deliver bursts of energy under rapid charge/discharge cycles due to their very high energy per unit volume or mass. Two types of supercapacitors are commercially available:

- Electrostatic double-layer capacitors (EDLC) have the highest energy density and capacity per volume, with a high-rate charge-discharge capability. Furthermore, the absence of any chemical reactions warrants a long lifespan. EDLCs store energy through electrostatic adsorption of the ionic species at the electrode-electrolyte interface, where the separation of charge takes place through a Helmholtz double-layer formation [86, 87].
- Electrochemical pseudocapacitors have redox-active material electrodes, such as metal oxides, where reversible faradic reactions occur. The pseudocapacitance is mainly achieved through faradic processes, including electrosorption, redox reactions, and intercalation, and only minorly through EDCL mechanism [88, 89].

Several companies are key players in the supercapacitor market (for both EDLC and ultracapacitors) [90], including Maxwell Technologies (United States) [91], Kyocera AVX (United States) [92], Panasonic (Japan) [93], Nippon Chemi-Con (Japan) [94], Nichicon (Japan) [95], and Tokin (Japan) [96] to mention some.

Functional Fluids

Ionic liquids are excellent candidates as operating fluids in various industrial applications due to their thermal stability, low vapor pressure and compressibility, good lubrication, moderate viscosity, and non-hazardous nature.

Lubricants

The potential of using ILs as specialty lubricants either under their pure form or as oil additives has been addressed since the early 2000s [97]. Their thermal stability and conductivity, low vapor pressure, low flammability, and dipolar structure, make them suitable lubricants. Additionally, certain atoms present in the IL composition (e.g., N, P, F, and B) are active reaction sites for the metals resulting during the friction process, potentially generating antiwear compounds [98].

Currently, two classes of ILs on the market are sold as lubricants: the electro-conductive lubricant from Klüber (Germany) and the high-pressure gas compression lubricant from Proionic.

Klüber Lubrication developed electro-conducting lubricants designed to protect the electric motors' rolling bearings from premature surface wearing caused by electrical arcing [99]. With the automotive industry transitioning from the 12 V to 48 V standard, stronger electric fields