

Ionic liquids „in a nutshell” (history, properties and development)

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Introduction

One of the main directions of the global research is the search for new chemical compounds with special properties. Ionic liquids are such compounds. Their application brings new possibilities for modern chemical technology. The ionic liquids fit well in the assumptions of green chemistry [1]. In contrast to the previous approach, the green chemistry requires design, development and implementation of new processes and chemicals that allow the reduction or elimination of use and production of hazardous materials [1]. Twelve principles of green chemistry, formulated in 1998 by Anastas and Warner [2], describe the methods of implementation of these tasks. Ionic liquids meet at least three of these principles, i.e. principle no. 5 (safer solvents), no. 6 (provide energy efficiency) and no. 9 (are used in catalytic reactions).

Ionic liquid precursors are quaternary ammonium halides, known from the 1890s, which were widely used and tested in the 20th century. The history of synthesis and application of organic salts containing a quaternary nitrogen atom is presented in Table 1.

Table 1

The history of the discovery and use of quaternary ammonium salts

Year	Practical use	Creators
1890	Synthesis	Menschutkin
1916	Bactericidal properties	Jacobs
	Surface active properties	
1935	Disinfection	Domagk
1960s	Fabric softener	
1960	Phase transfer catalysis	Jarousse-Mąkosza
1970s	Antielectrostatics	
1977	Wood preservation	Butcher <i>et al.</i>
1980s	Asphalt modifiers	
1990s	Clay modifiers	
1996	Ionic liquids	Seddon, Rogers

Ionic liquids (ILs) are defined as chemical compounds of ion structure, which have the melting point below 100°C [3, 4]. This property is usually a result of a large size difference between an organic cation of expanded asymmetric structure and a small organic or inorganic anion. This hinders the formation of a uniform crystal lattice, thus greatly reducing the solidification point of the compound [5, 6]. Figure 1 presents a general model of an irregular system of ions in the IL structure.

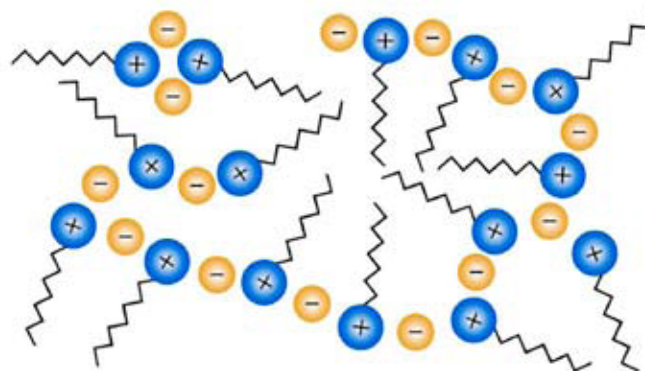


Fig. 1. Simplified model of an IL

From the beginning of the 20th century, Chemical Abstracts use two keywords to describe these compounds: *room-temperature ionic liquids* (RTILs) and *ionic liquids* (ILs) that apply to liquid and solid salts, respectively, at room temperature. Currently, such keywords as *molten salt*, *liquid organic salt* or *fused salt* are no longer used to describe ionic liquids. Generally accepted abbreviations are ILs and RTILs. In the Polish literature, an English abbreviation (ILs) is usually used, but sometimes also a Polish abbreviation (C), from Polish *ciecz jonowe* can be encountered. We recommend using the English abbreviation (IL) for standardisation purposes, since the English language is predominant in the chemical literature. Mark it in the first citation (IL).

History of ionic liquid

To search for the origins of research on ionic liquids, one has to look back to the mid-19th century, when a low-melting organic salt has been observed for the first time. It was a by-product produced in the reaction of benzene alkylation in the Friedel-Crafts reaction, with aluminium chloride as a catalyst. The “red oil”, as at the time the substance was called, had remained unidentified for over 100 years. Only after the popularisation of nuclear magnetic resonance technique, it was possible to identify its structure (Fig. 2) [7].

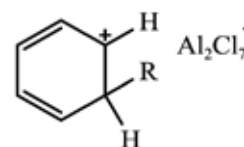


Fig. 2. Chloroaluminate, σ -complex in the Friedel-Crafts reaction

At the turn of the 20th century, the first reports on low-melting salts were published. In 1888, Gabriel and Weiner obtained ethanolanmonium nitrate with the melting point of 52°C [8]. In 1914, an ethylanmonium nitrate was described (melting point 12°C) [9], considered the first low-temperature ionic liquid. Therefore, Walden is considered as a „father” of ILs. This is contested by Everts [10] who quotes Boeck on the fact that the Walden’s paper indeed

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discussed conductivity of ethylammonium nitrate, but their author did not recognize its potential application. Moreover, Boeck states that six years before Schall, a Ostwald's (Nobel laureate in 1909) student had published a paper on organic salts with a low melting point, which are nowadays classified as ILs [11]. However, this discovery was not found interesting in scientific circles. It may be assumed that an important reason for that was their poor solubility in water, which was at the time considered a universal solvent.

The 1950s brought interest to organic liquid salts. In 1963 Yoke described a reaction of copper(I) chloride with triethylammonium hydrochloride, which gave a liquid product [12]. The progress in IL studies was particularly impacted by the series of studies conducted in the 1960s and 70s at the U.S. Air Force Academy by King and his co-workers – Wilkes and Carlin. These studies aimed to find an electrolyte for the thermal battery. Based on patents from 1948 [13], a cell was developed containing an ionic liquid produced in the reaction of aluminium chloride with 1-ethylpyridinium bromide as an electrolyte [14]. On the other hand, Koch's research team used 1-ethylpyridinium chloroaluminate as a solvent in catalytic reaction [15]. 1-Butylpyridinium chloroaluminate to be more effective, and melted at 40°C [16]. Even better results were obtained for the 1,3-dialkylimidazolium cation. Combining 1-ethyl-3-methylimidazolium chloride with aluminium chloride gave RTIL [17]. In 1986, a research team under the leadership of Wilkes used it as a solvent in the Friedel-Crafts reaction, thus proving its catalytic activity at the same time [18]. It was observed that pyridinium, as well as imidazolium chloroaluminates, break down in the presence of water with the exudation of gaseous hydrogen chloride and are even sensitive to atmospheric moisture [7]. As a consequence, their application was burdensome, because their processing required the anhydrous conditions. Replacing a chloroaluminate anion with another anion resulted in obtaining ILs that were completely stable in contact with an aqueous solution. 1-Ethyl-3-methylimidazolium ILs, insensitive to water, were synthesised using inorganic (BF_4^- , NO_3^- , SO_4^{2-}) and organic (CH_3COO^-) anions [19].

The increased interest in ILs in the last two decades was caused by several factors. Ionic liquids quickly started to be considered a "green" alternative for volatile, flammable and often toxic popular organic solvents. The ILs have been recognized as more environmentally friendly solvents and catalysts, and at the same time their unique advantage, i.e. designability, has started to be appreciated. ILs can be designed by selecting a proper cation and anion to obtain a compound with desired properties. In this way it is possible to synthesise ILs for a specific application [20]. The term was coined in the literature for such type of compounds – task-specific ionic liquids (TSILs). The name was approved by academic circles after Davis' publication in 2004 [21]. The number of possible combinations of a cation and anion was estimated to be at level of 10^{18} [22]. Such a great diversity makes it possible to design a structure that will provide optimum properties for very specific purposes. This directly translates into a potential application of ILs in various technological processes [3, 23]. In 2002, BASF, as one of the first companies, has implemented a technology based on ILs (BASIL™ – Biphasic Acid Scavenging Utilizing Ionic Liquids™) [24].

Properties of ionic liquids

There is a number of unique properties related to the ionic structure of ILs, which in combination with the liquid state in a wide range of temperatures, determines their technological usefulness. Their advantages include virtually non-measurable vapour pressure under moderate conditions [25]. This has a positive effect on their safety as solvents, and eliminates atmospheric vapour emission. No volatility, in combination with moderately low flammability of ionic liquids, greatly reduces fire or explosion risk, as opposed to traditional

organic solvents. The majority of ILs exhibit high thermal stability. The vast majority is inflammable [26]. However, caution is advised as their decomposition products may ignite [27]. This property has been used in the development of energetic ionic liquids [28].

ILs are conductive – they are applied as electrolytes. The conductivity is usually in a range of 0.1 to almost 20 mS. High conductivity is typical for liquids with an imidazolium cation and weakly coordinating anions, e.g. a tetrafluoroborate anion [29]. At the same time, ILs are electrochemically stable in a wide range, usually of 4.5–5 V [30], which enables their use as electrolytes and modifying agents for electrochemical processes. Recently, there was an interest in ammonium ILs containing a chlorine atom in an alkyl substituent [31].

Year 2002 brought a publication of a breakthrough report on dissolving cellulose in ILs without any auxiliary substances [32]. Attempts to ascribe the discovery of cellulose solubility to the papers published before 2002 are unfounded. The issue was precisely clarified by McCrary and Rogers [33]. This opened new possibilities in biomass processing and contributed to an intensified research on biopolymer solubility in ILs [34]. The studies conducted led to the conclusion that cellulose is soluble in imidazolium and ammonium ILs, which mainly contain acetate anions and short alkyl substituents at a quaternary nitrogen atom. The incorporation of the alkyl substituent with a higher number of carbon atoms into the cation structure results in visible reduction in cellulose solubility, up to non-solubility, with gained bactericidal and fungicidal activity. A limiting substituent, for which the IL stops dissolving cellulose and gains biological activity, is octyl [35].

Due to their ionic structure, ILs have low volatility (non-measurable vapour pressure) at ambient temperature. The following question often arises: Why do certain ILs have characteristic smell? An unpleasant odour of the product depends on impurity (usually of an original substrate). For ammonium ILs, for example, amine serves as a substrate, which has the odour threshold at a very low level. Amine content is at a level of ppm. It can be completely removed, but due to time required and profitability, it is usually neglected or intentionally disregarded.

ILs have surprising functional properties. For example they can be used to preserve soft tissue [36], as feeding deterrents [37] or rubber accelerators [38], which motivates their further research. Never before in the history of chemistry has there been such a large research system with available substrate sources (both cations and anions). For many ionic liquids we have detailed knowledge about their availability, price, physicochemical and biological properties, including toxicity and ecotoxicity. Biomass can also serve as an ion source. ILs synthesised in this manner are known as *bioionic liquids* [39]. We have joined this field of research by synthesising ILs with a natural anion [40, 41] and herbicidal ionic liquids from renewable sources [42, 43].

Classification of ionic liquids

It is difficult to classify the previously described ionic liquids, as there is no single criterion allowing it. A partial solution is to classify them based on the physical differences of a cation and anion, or on their potential applications.

Liquid state of ILs at relatively low temperatures is caused by the presence of structures hindering crystallisation in their structure. These include hydrogen bonds between a cation and anion [44–46] and a large size and strong asymmetry of an organic cation [47–49]. We present ILs containing a cation, in which the positive charge is located on a nitrogen, phosphorus, sulfur or oxygen atom. This is why they are divided into ammonium, phosphonium, sulfonium and oxonium ionic liquids. So far, ammonium liquids are best known, whereas the least known are oxonium ones, as a large number of them is metastable [50]. The principle of the general classification based on the type of an atom with a positive charge is presented in Figure 3.

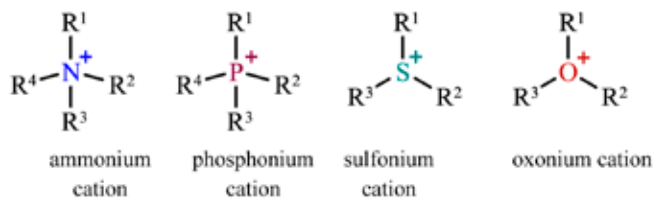


Fig. 3. Types of cations

The cation may have one or more atoms with a positive charge [51]. An example of such ILs are trigeminal tricationic ionic liquids, i.e. cations that have three positively charge nitrogen atoms. ILs with such structure (Fig. 4) can be obtained by chloromethylation of glycerol, followed by quaternisation and substitution reactions [52].

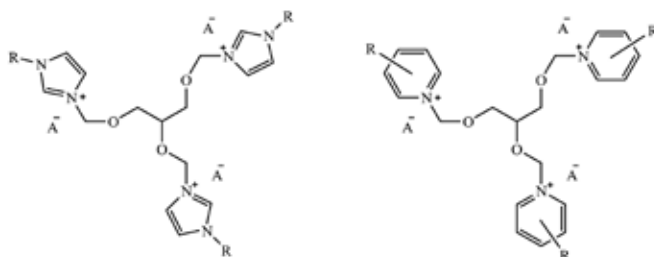


Fig. 4. The structures of imidazolium and pyridinium triplets

The cation classification is also affected by more subtle differences in the structure. A positively charged atom may have separate, not interconnected alkyl substituents, which determine great diversity of such cation conformations and directly affects its physicochemical properties [53]. Such cations are known as aliphatic. Heterocyclic cations are the opposite. In this case, each charged atom is a part of a cyclic or polycyclic group with condensed rings. Among heterocyclic ammonium cations, two structure subtypes can be distinguished depending on the hybridisation of a charged nitrogen atom. By means of this criterion, heterocyclic cations may be divided into cations containing heteroatom of sp^2 hybridisation (aromatic heterocyclic cations) and sp^3 hybridisation (non-aromatic heterocyclic cations). Example structures are presented in Figure 5.

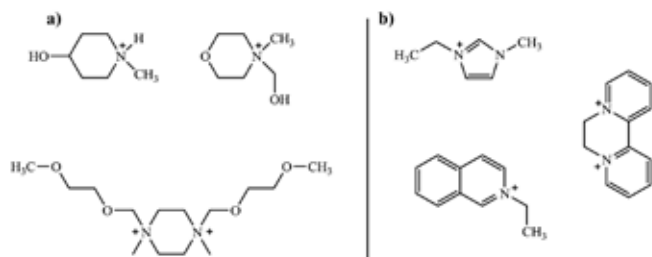


Fig. 5. Heterocyclic non-aromatic (a) and aromatic (b) cations

Regardless the element that is positively charged in the cation structure, the following classification criterion is distinguished. If the positively charged atom is chemically bonded with at least one hydrogen atom, the salts of such structures are known as protic ionic liquids (PILs) [54]. The presence of the hydrogen atom at a central cation atom leads to the formation of a network of strong supramolecular hydrogen bonds, which are characteristic for PILs [55]. However, if the positively charged atom is not bonded with any hydrogen atom, i.e. it has the maximum order, such an ionic liquid is called an aprotic ionic liquid (AIL) [56]. Examples of aprotic and protic ionic liquids are presented in Figure 6.

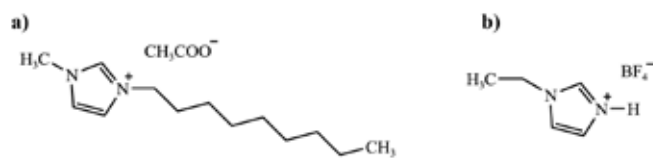


Fig. 6. Sample structure AIL (a) and PIL (b)

ILs differ greatly in terms of their physicochemical and biological properties, which results in even greater number of potential applications. A general and useful criterion was created in 2007. Based on IL designability, the existing ILs were divided into three generations (Fig. 7) depending on the type of properties provided by the structure of a cation and anion [57]. The generations are ordered according to the “evolution” history and studies of ILs.

The 1st generation includes ILs in which the cation and anion structures were chosen to obtain a product of specific physical properties. The effect of the cation or anion structures on conductivity is of special importance as it translates into their specific applications as electrolytes [58]. Ions of the 1st generation ILs were also selected to achieve specific values of melting point, density, viscosity, thermal stability, hydrophilicity and refractive index [57].

The usefulness of the 2nd generation ionic liquids is a result of both suitable physical parameters and chemical properties. The latter includes their reactivity, chirality [59], solvating ability and ability to extract various chemical substances [22]. This group includes TSILs, energetic ILs [28] and chemical reaction catalysts [18, 60].

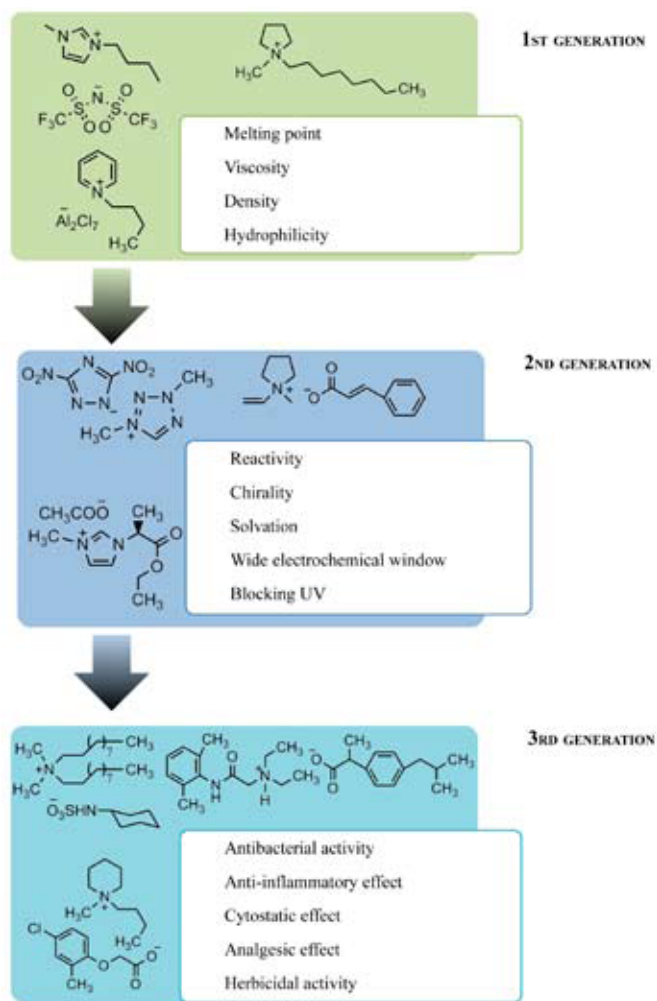


Fig. 7. Generations of ionic liquids

Dynamically growing knowledge of ILs resulted in the creation of the 3rd generation of ionic liquids in the early 21st century. It includes compounds that apart from selected physicochemical properties also

exhibit a specific biological activity. One of the first 3rd generation ILs were salts of a strong bactericidal effect [61]. The ions of pharmaceuticals used serve both as cations and anions of the 3rd generation ILs, acting against pain and anti-inflammatory [57, 62]. This generation also includes plant protection products, including protic derivatives of triazoles showing fungicidal activity [63] and herbicidal ionic liquids (HILs) such as derivatives of phenoxyacids exhibiting a selective herbicidal activity against dicotyledonous plants [64].

The biological activity may be achieved by both cations and anions, which enables the synthesis of the multifunctional 3rd generation ILs [65]. The HILs described to this day contain anions of the following herbicides: 2,4-D [66, 67], MCPA [64, 68], MCPP [69], MCPB [70], dicamba [71, 72], fomesafen [73], glyphosate [74], clopyralid [75], metsulfuron-methyl [76] and bentazon [77].

In the literature one can find terms describing the original properties of ILs, such as: energetic [28], sweet [78], chiral [57, 79], herbicidal [64] or coloured [80]. The spectrum of IL applications is so extensive that new terms will certainly appear.

Summary

The ionic liquids stopped being a scientific sensation and become the subject of intensive research conducted by scientific circles, research institutes as well as industrial centres. The most often synthesised ILs are new compounds without CAS RN assigned (*The Chemical Abstracts Service Registry Number*). Well-known and widely used chemical compounds are often used as a source of cations and anions. This prolongs the “life” of many useful organic compounds, which are often almost irreplaceable, but pose a threat to the environment, so such applications eliminate their undesirable properties.

ILs are multifunctional compounds – the anion-cation combination enables the synthesis of ILs that can successfully replace formulations composed of a few different compounds. In case of ILs, the natural environment is burdened by only one chemical compound, instead of several substances previously introduced – i.e. the ingredients of a commercial formulation.

Working with ILs guarantees both scientific and technological success. However, the outcome desired requires patience and a well-organised research workshop. A cooperation between research teams from various fields is also advisable, from organic chemistry, through electrochemistry, physical chemistry and analytical chemistry, up to chemical technology.

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RYNEK

Grupa PCC EXOL – wyniki z dużą „górką”

Grupa PCC EXOL zakończyła I półrocze z rekordowymi wynikami finansowymi. Grupa specjalizuje się w produkcji zróżnicowanych produktów chemicznych znajdujących zastosowanie zarówno w detergentach, kosmetykach jak i w specjalistycznych produktach przemysłowych. Zysk EBITDA ukształtował się na poziomie 24,3 mln PLN (+35,2% H/H), zysk netto wzrósł o 6,9 mln PLN do 12,4 mln PLN (+124,2% H/H). Przychody ze sprzedaży osiągnęły poziom 265,9 mln PLN (+5,2% H/H). Wzrost zysku netto to konsekwencja przede wszystkim wzrostu marży na sprzedaży do poziomu 17,5% (+2,6 p.p. H/H) oraz poprawy wyniku na działalności finansowej o 1,8 mln PLN (+30,1% H/H). Wyższe przychody ze sprzedaży w porównaniu do I półrocza 2015 r. to głównie efekt zwiększonej sprzedaży wysokomarżowych surfaktantów do zastosowań przemysłowych, których sprzedaż Grupa konsekwentnie rozwija. Zwiększenie ich udziału w strukturze sprzedaży wpłynęło także na wzrost marży na sprzedaży. (kk)

(<http://www.pcc-exol.eu/>, 29.08.2016)

Epidarex Capital zakłada spółkę Nodthera Limited, która będzie wykorzystywać wyniki badań Selvity

Selvita SA, największa innowacyjna firma biotechnologiczna w regionie Europy Środkowo-Wschodniej oraz Epidarex Capital, ogłosiły powstanie nowej spółki biotechnologicznej Nodthera Limited, która skupi się na odkrywaniu i rozwoju innowacyjnych inhibitorów inflamasyonu NLRP3. Działalność spółki Nodthera będzie oparta o światowej klasy badania, jakie prowadzone były do tej pory przez Selvitę. Głównym inwestorem w spółce Nodthera jest Epidarex Capital, wiodący fundusz typu *venture capital* inwestujący w przedsięwzięcia na wczesnym etapie w branżach wysokiego wzrostu, takich jak *life science* oraz technologie medyczne. Międzynarodowy zespół zarządzający funduszem Epidarex ma udokumentowane doświadczenie we współpracy z najlepszymi naukowcami i przedsiębiorcami, mającej na celu rozwój wysoce innowacyjnych produktów dla światowego rynku opieki zdrowotnej. Jednym ze współników w Epidarex Capital jest Eli Lilly, wiodąca globalna firma farmaceutyczna. Główna siedziba spółki Nodthera znajduje się w Edynburgu, w Szkocji. (kk)

(<http://biotechnologia.pl/>, 4.08.2016)

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