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Journal of Pharmaceutics and Pharmacology Research
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Mini Review

Ionic Liquids Nitrogen-Based, Preparation, Characterization, and Application

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Received Date: April 02, 2022; **Accepted Date:** April 20,2022; **Published Date:** May 04,2022

Citation: Rabei Seliman, Sahl Yasin, and Mohammed S A Eltoum, (2022). Ionic Liquids Nitrogen-Based, Preparation, Characterization, and Application. Journal of Pharmaceutics and Pharmacology Research. 5(6). DOI: 10.31579/2693-7247/083

Abstract:

Nowadays Ionic Liquids (ILs) salts becomes a major class of attention due to their numerous industrial applications in various fields such as softest solvents, catalysts, batteries, wastewater treatment…etc. In this review, we highlight and present ionic liquid nitrogen-based in both aliphatic and aromatic compounds. Aliphatic based nitrogen ionic liquids are prepared from different sources like trimethylamine, diethylamine, triethylamine, -tripropylamine, iso-propylamine, n-tributylamine, and n-butylamine. However, to prepare aromatic based nitrogen ionic liquids, it's better to use amidazole, Quinine, pyridine, Pyrrolidin, Pyrrol and Piperidine. A set of physicochemical methods used to characterize ionic liquids such as UV, FTIR, NMR, and TGA are used for thermal investigation. It can be seen that during ionic liquid preparation some impurities remain such as negative radical impurities. This review shows an opportunity to understand ionic liquids preparation from different sources, stability, characterization and their main application.

Keywords: ionic liquids; nitrogen based; imidazole

Introduction

Ionic liquids are salt composed of unsymmetrical segment's organic cations and inorganic anions. They can be used as a green solvent as well as catalysis due to their unique properties, such as their high-thermal stability, very low flammability, high electrical conductivity, highly polar, miscibility with a wide range of organic solvents, and negligible vapour pressure [1]. Depending on the cationic segment the ionic liquids can be named and categorized as further; imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, pyrrolidinium, cholinium, sulfonium, picolinium, piperidinium, thiazolium, triazolium, guanidinium etc, However, inorganic anions such as acetate, trifluoroacetate, tetrafluoroborate, hexafluorophosphate or bromide anions can be negative radicals [2]. Or by chemically modifying either the cation or the anion.

In 1914 a low melting-point salt (ethylammonium nitrate) was discovered by Paul Walden, from that time at least approximately 10^6 ionic liquids salts had been prepared easily from different sources. (Citation Yun Deng). Due to the dual nature of ionic conductivity and glass-forming wild range of ILs have been prepared, which open up for good nature of ILS as supercooled liquid and glassy states area [3].

Ionic liquid can be prepared easily by ammonium, imidazolium or phosphonium as cations; while, anions as sulphate, phosphate, fluoride, thiocyanate and carboxylate.

The main goal of this is studied to review and demonstrate ionic liquid-based nitrogen, as green tools solvent.

Preparation of aliphatic Ionic liquid ammonium-based

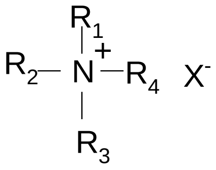
Ionic liquids based nitrogen was prepared easily by direct reaction of non-aromatic amines and acids.

The simple ionic liquid can be formed as {amine}{X}. Researchers used trimethylamine, diethylamine, triethylamine, -tripropylamine, iso-propylamine, n-tributylamine, and n-butylamine, as back pone materials for cationic radical, while X represent anionic radical. X= $H_2PO_4^-$,BF_4^-, HSO_4^- and CH_3COO^- …etc.

Ionic liquid	Chemical formula	Start materials	Reaction condition
Triehylammonium dihydrogen phosphate	$[Et_3NH][H_2PO_4]$	H_3PO_4 with triethylamine	60℃ for one hour
Triethylammonium sulfate	$[Et_3NH][HSO_4]$	H_2SO_4 with triethylamine	60℃ for one hour
Triethylammonium tetrafluoroborate	$[Et_3NH][BF_4]$	HBF_4 with triethylamine	60℃ for one hour
Triethylammonium Acetate	$[Et_3NH][CH_3COO]$	CH_3-COOH triethylamine	60℃ for one hour

Table 1: *simple ionic liquid ammonium-based*

Table 1 summarizes the preparation of simple ionic liquids ammonium-based. It can be seen that the yield and conversion of HSO_4^- is better than other radicals H_2PO_4, BF_4, and CH_3COO^-, on other hand, cation radicals, dosage and temperature influence the yield percentages. (4) (5). Novel ionic liquids nitrogen-based have been synthesized and characterized by Weng et al 2005 a general formula is followed [amine] $[HSO_4]$. Di and Tri ethylamine mixed with H_2SO_4. The reaction formed white crystalline powder after the kept temperature at 0 ℃ (6)



$R_{1,2,3}$= H, Me, Et, Pr, Bu; X=H_2PO_4, HSO_4, BF_4

Figure 1. *The structures of simple ammonium ionic liquids.*

Heterocyclic Ionic Liquid-Based Nitrogen

Heterocyclic ionic liquids nitrogen-based were classified into six main types due to nitrogen position; imidazolium, pyridinium, pyrrolidinium, piperidinium, guanidinium and quinolinium. They can be abbreviated as Im, Py, Pyr, Pip, Gu and QuⅡ, respectively.

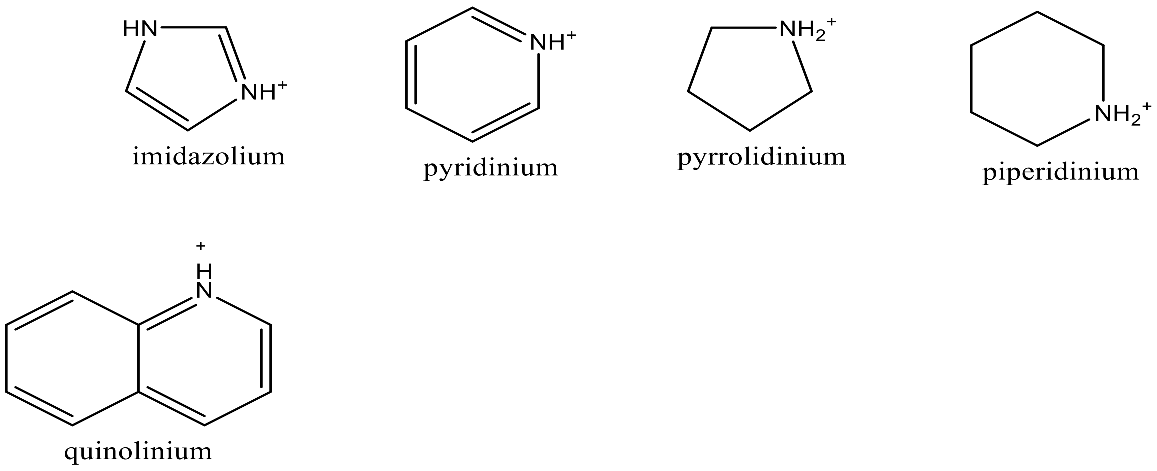


Figure 2: *Heterocyclic ionic liquids based nitrogen*

Imidazolium

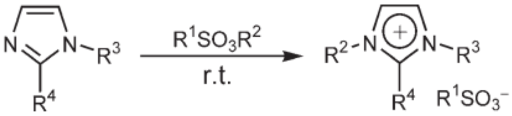
In 1858 DEBUS discovered the first methods for preparing amidazole from ammonia and glyoxal (1,2-dicarbonyl). It had been introduced to industrial by HANTZSCH in 1950, from that time a wide range of derivatives is now available for industrial. Radziszewski`s reaction is considered to be a famous method for producing imidazoles [3].

It can be started from the treatment of alcohols with alkanesulfonyl chlorides in the presence of a base such as triethylamine affords the pure alkyl sulfonate esters due to their easier and possibility to use different R_1 and R_2 groups and thus generate a large variety of 1, 3-dialkylimidazolium alkanesulfonate Salts. The alkylation of N-alkylimidazoles such as N-methylimidazole with the alkyl sulfonate can be generated in without solvent conditions at room temperature affording the corresponding1,3-dialkylimidazolium alkanesulfonate salts as crystalline solids in almost quantitative yield [7]

Equation No1.

$$R^2OH \xrightarrow[NEt_3,rt]{R^1SO_3Cl} R^1SO_3R^2$$

Equation No.2



Quinolinium

Quinine was extracted from the bark of cinchona trees, its attractive starting material for its stability, flexibility and availability in nature. To increase the stability of quinine as aromatic quinolinium ionic liquids and install a positive charge nitrogen atom can be alkylated under basic conditions. The results indicate that the quinuclidine cation is relatively stable under basic conditions, unlike many traditional ionic liquids. Quinine derivative salts maintain high melting points due to various functional groups: an aromatic ring, a terminal double bond, a methoxy group and an OH group. Several of the salts decompose rather than melt. Most of the researchers argued that quinine cation would suffer from base instability and be difficult to derive directly from a natural molecule. Preparation of ionic liquid-based quinine usually begins with the quaternisation of a saturated Lewis base with an alkyl halide, followed by ion exchange. Always the alkylation was fulfilled in methanol (MeOH) prevents overalkylation, acetonitrile, using (MeCN) to provide a higher yield of 64%, and preparation of [MeQn] by using methyl tetrahydrofuran (Me-THF) gave only 38 % yield [8]

Pyridinium

Pyridinium is found in nature as secondary metabolites in; marine sponges, it may be found as primary metabolites such as nicotinamide adenine dinucleotide (NAD+). Pyridine and functionalized pyridine have been introduced in the preparation of ionic liquid. Hydroxyl functionalized pyridinium ionic liquids have been prepared by C. D. Roux and his co-work, furthermore, they used alkylpyridines to prepare N-(2-hydroxyethyl)-pyridinium ILs under a bromide salt. Physiochemical properties are determined such as density, viscosity, conductivity, and thermal decomposition temperature, therefore, their result meets theoretical calculations [9]. Computational measurements were used to calculate the effect of involved inions and cations on pyridinium ionic liquids, viscosity was analyzed during calculation, however, it assists by quantum, density functional theory, and classical molecular dynamics simulations. The computational experimental results showed that there was a complex effect controlling the viscosity of studded parameters such as the strength of ionic pairs, molecular sizes, and mobility of pyridnium based ionic liquids [10]. In addition, N-functionalized pyridinium scaffolds as a single electron, redox-triggered functional group transfer reagents [11]

Pyrrolidinium

Pyrrolidin stands on the five-membered nitrogen-containing ring. Researchers used to prepare pyrrolidin from different sources, pyrrolidin-1-oxyl–(nitronyl nitroxide)-dyad and pyrrolidin-1-oxyl–iminonitroxide-dyad had been prepared under controlled temperature and magnetic susceptibility [12]. Furthermore, pyrrolidinium and piperidinium based ionic liquid and linked to platinum compounds ([Pt(cod)Cl_2] and K_2[PtCl_6]) they applied as catalysts for hydrosilylation 1-octene and allyl glycidyl ether with 1,1,1,3,5,5,5-heptamethyltrisiloxane [13]. Burrell et all discover a new method for producing large quantities of high pyrrollidinium based ionic liquids. The experiment started by alkylation of methylpyrrolidine under cool conditions. The results showed that pyrrolidinium ionic liquid salt is more stable than imidazoles IL salts.

Piperidinium

Piperidine structure contains $C_5H_{11}N$ (Hexahydropyridine, perhydroazine). It was isolated from alkaloid piperine which occur in black paper *piper nigrum* [14]. Recently, 2,2,6,6-Tetramethylpiperidine-1-yloxyl derivatives were investigated after being substituted with hydrogen and ionic radicals such as [$-OSO_3^-Na^+$, $-OSO_3^-K^+$, …etc] Their viscosity has been described by Vogel–Fulcher–Tammann equation, therefore, well determination of the dependence of the spin density on nitrogen on the substitution pattern of the 4-position of the probe was described by quantum chemical calculations of the spin probes [15]. The phase diagrams for the binary systems of {1-butyl-1 methylpiperidinium thiocyanate} and {1-ethyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl imide} have been prepared under influence of alcohol. Their solubility is checked under the increase of the alkyl chain length of alcohol. Meanwhile, (Solid + liquid) phase equilibria with complete miscibility in the liquid phase region were demonstrated [16].

Characterization

A set of physicochemical methods is used to characterize ionic liquids such as UV, FTIR, NMR, and thermal characterization like TGA. It can be seen that during ionic liquid preparation some impurities remain such as negative radical impurities like chloride, sulphate and water and/or other solvents. Most of the imidazolium based ILs salt shows important absorption in the ultraviolet (UV) region and long tail in the visible region due to extended hydrogen bond and other functional groups attached to it, which recorded at weak absorption around 300nm [17]. 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium acetate spectra were checked at 190 and 260nm respectively in UV regions [18]. Imidazolium based RTILs show different absorption in IR spectra due to the relative position of the anion concerning imidazolium cation. Structural factors like the position of cation and anion determine the physical and chemical [19]. The main feature in the IR spectra is the characteristic functional groups such as C≡N vibrations. The C≡N vibrations decrease in wavenumber as the length of the alkyl chain increases, i.e., from 2261 cm^{-1} in 1a to 2241 cm^{-1}, however, The IR spectra exhibit C-H bond stretches between 3150 and 2950 cm^{-1} and weaker C-H bond stretches between 2850 and 2460 cm^{-1}, possibly arising from the formation of hydrogen bonds with the anion [20].

High-performance NMR is used to detect ionic liquid salts. It May help to reveal the liquid state structure and reactivity of the solvent, allows for process and purity control in industrial environments, and open a way toward in situ investigations of reactions in ionic liquids [21]. Single-crystal X-ray diffraction analysis was used to reveal an extensive series of hydrogen bonds between H atoms on the cation and the anion. This technique presents the crystal type of ionic liquid as well as the bond Lengths [20]

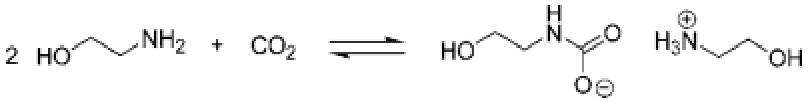
Application:

The ionic liquids are used in wild range applications, in catalysis, as solvents, in solar energy, heat transfer, power storage, etc.

Ionic liquids based nitrogen is used as a catalyst in cracking reactions for eliminating dialkoxypropanes as alternative traditional volatile solvents, the results clearly showed that ionic liquid can be separated and reused without losing their activity and quality. Furthermore, the yield, conversation, and selectivity of this method are better than traditional methods. [6]

At room temperature, some ionic liquids based nitrogen has novel applications for minimising and reversible Capture of CO_2 (see Scheme 1). The process took place by using mono and di ethanolamine. Aforementioned ionic liquids are capable to capture carbon dioxide due to amine functional groups, under the condition of low temperature and pressure. [22]

On other hand, a new novel liquid porous materials with tetrahedral coordination cage have been prepared from ionic liquid-based nitrogen,



Scheme 1. Reversible Reaction of CO_2 with 2 equivalent of MEA to Form a Carbamate Salt

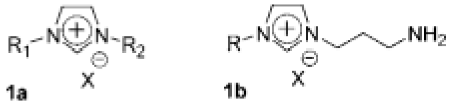


Figure 1. *General structures of (a) imidazolium-based RTILs and (b) amine substituted "task-specific" ionic liquids (TSILs).*

Figure 2. *RTIL solvents for alkanolamines in CO2 capture*

Imidazole-based ionic liquids have found uses in potential water treatment agents due to their ability to coordinate with metal atoms, also recognized for their potential as green organic solvents due to their lack of volatility [23]

Ionic liquids are used to reduce pharmaceutical residues from the environment, Potential of ILs as pharmaceutical solvents for solubilizing poorly soluble pharmaceutical active ingredients (APIs) has been reported. In addition, their use as a drug delivery vehicle was investigated. AP-IL provides multiple ways to modify the chemical and physical properties of an API (melting point, chemical stability, physical stability, solubility, bioavailability, dissolution rate, etc.) with a relatively simple approach. It is attractive to the pharmaceutical industry. Additionally, it permits a synergetic movement upon the perfect choice of the counter-ion. API-ILs counter-ions which might be appropriate for pharmaceutical use continue to be to be completely enumerated, however over 370 materials are indexed as "Generally Regarded As Safe (GRAS)" through the FDA (U.S. Food and Drug Administration), which includes vitamins, meals components and different well-well-known materials. Additionally, incredibly secure drugs, inclusive of paracetamol and aspirin, also are legitimate counter-ions. (24). Some problems are related to solid drugs. Polymorphic, metastable and poor water solubility is a major issue that can affect bioavailability. Development Ingesting the active ingredient salt is one of the strategies to overcome these problems. Since 2007 there is growing interest in the development of room temperature ionic liquids (RTILs). uses active pharmaceutical ingredient (AP-IL) (25). Numerous studies show that a wide variety of pharmaceuticals are present in wastewater effluents and are a matter of great concern for public health.

Conclusion

In this review, nitrogen-based ionic liquids were presented and deep analyzed, for forming ionic liquids. Two kinds of materials based on nitrogen are used as start sources aliphatic and aromatic. It has been seen that the preparation of IL is done in two different parameters; room temperature and from 60 and 100℃. One of the problems with using ionic liquids in chemical applications is that the viscosity of IL decreases at high temperatures. As a result, IL becomes fluid lost.

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DOI: **10.31579/2693-7247/083**