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LATEST DEVELOPMENT ON THE METHODS OF SYNTHESIZING IONIC LIQUIDS

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Abstract – Nowadays, in spite that the application of ionic liquids in some domains is still at infancy stage, the related synthetic technologies have got tremendous development over one century. In this paper, we made an overview on characteristics of five approaches to synthesize ionic liquids and compared the advantages and disadvantages of different methods, and gave recommendations for the best means of synthesizing to the objectives of related studies. Finally, the present work provides a full-scale literature review of the implementation of synthesizing ionic liquids, which could assist the corporations or individuals to search for the most suitable methods and lay the foundation for exploiting more ideal methods to obtain high purity and better yields of ionic liquids in the future.

1. INTRODUCTION

Ionic liquids (ILs) are usually known as room temperature molten (melting point <100 °C) salts or deep eutectic solvents.[1] In general, ILs are composed of large unsymmetrical organic cations, such as pyridinium ion, imidazolium ion, pyridazinium ion, pyrrolidinium ion, ammonium ion, phosphonium ion, etc., and relatively smaller inorganic or organic anions, which include Cl^-, BF_4^-, PF_6^-, $AlCl_4^-$, ClO_4^-, $[N(OTf)_2]^-$, $[CF_3CO_2]^-$, $[CF_3SO_3]^-$, $[PhCO_2]^-$, $[N(CN)_2]^-$, $[RSO_4]^-$, $[OTs]^-$, $[SCN]^-$, NO_3^- and so on.[2]

ILs, being proud of their excellent physicochemical properties, such as negligible vapor pressure, thermal stability, high ionic conductivity, good designability, etc., have attracted a lot of attention during recent years, especially in the green chemistry area. Therefore, as an eco-friendly reaction medium, ILs have been widely applied to the field of organic synthesis, electrochemistry, extraction and separation, biocatalysis, etc.[3]

Ethylammonium nitrate $[EtNH_3][NO_3]$, as the firstly synthesized ionic liquid in 1914 by Walden occasionally,[4] did not obtain adequate attention at that time. Organic chloroaluminates, first mentioned in

1951 and studied in detail from the 1970s onwards, are now considered to be as the first generation of ILs. However, owing to rapid hydrolysis, such salts were produced in an atmosphere filled with inert-gas.[5] Since the 1990s, this kind of compounds consisted of ions have started to draw universal attention, the publication rate of relevant literatures about ILs also dramatically increased indeed.[6]

The first appearance of ionic liquids provided a useful extension to the range of solvents that are available for synthetic chemistry. Whereas the synthesized process needs lots of time, in addition to a quantity of energy. Unceasing appearance of a series of new synthetic methods, which include microwave and ultrasound irradiation, electrochemical and extraction method, substituted for traditional heating technique as for their obvious merits, such as short reaction time, better production yields, scale-up of reactions and high purity outcomes.

In this article, we examined the scientific literatures and summarized respective characteristics of methods for synthesizing ILs. In addition, we compared the advantages and disadvantages of each method, to help search for optimal method to meet different application requirements.

2. THE SYNTHETIC MECHANISM OF ILS

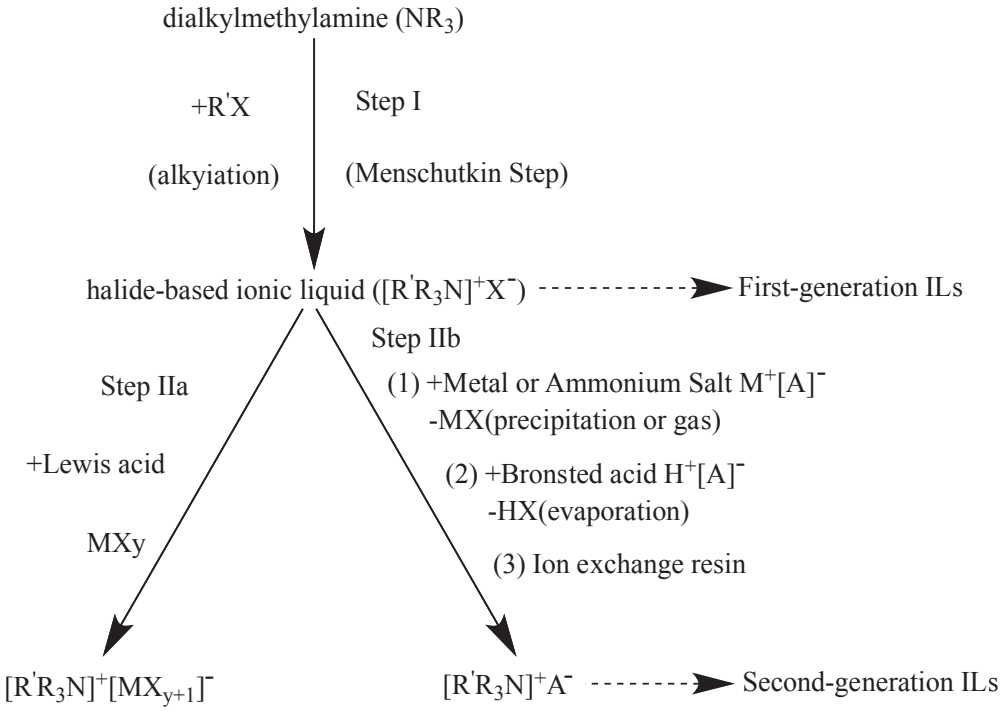


Figure 1. Two different approaches to carry out ILs

Generally speaking, the primary method for preparing ILs can be described as two successive steps, namely, formation of desired cation and exchanging of counter-anion.[7] As shown in Figure 1, the first step affords the procedure of quaternisation based on alkylhalides and animidazole, pyridine, amine, etc.,

to produce the halide-based ILs (First-generation ILs). The second step mainly involves the progress of an anion exchanger, that is, the halide ion is displaced by other desired anion (BF_4^-, PF_6^-, $CF_3SO_3^-$, ClO_4^-, etc.), thus forms corresponding new ILs (Second-generation ILs).[8]

3. CONVENTIONAL SYNTHETIC METHODS

Massive classical reactions of ILs are conducted via employing conventional heating-reflux methods. In brief, the reflux device consists of the heating system, which is put into with a steady flow of thermal energy, and the cooling system, in which cool water is used for condensing boiling compounds.[9]

Despite the traditional synthesis method played a vital important role in the development of ILs, more and more drawbacks emerged obviously,[10] mainly shown in Table 1.

Table 1. Drawbacks of traditional synthesis method

	Drawbacks
I	Extra reaction reagents (acetone, toluene, acetonitrile, etc.) are needed;
II	Synthesis process is time-consuming;
III	Excessive of reactants are required to achieve good yields;
IV	Large volumes of organic solvents (ethyl acetate, ethanol, etc.) are necessary for products purification;
V	The products yields are relative low;
VI	Energy input are tremendous for heating and cooling.

To reduce solvent consumption or recycle used solvent, Aupoix et al. made some improvements in the traditional heating method using one-pot procedure, and successfully prepared ILs with solvent-free systems, although purification step sill needed solvents.[11] However, under increased pressure of "Green Chemistry", which emphasizes on twelve principles: atom economy, energy efficiency, minimum chemical waste, benign solvents, efficient isolation processes, sustainable synthetic method, safer catalysts & regents and renewable feedstock, it is in great need to develop available methods to overcome the disadvantages of conventional methods, the non-conventional synthetic methods showed up one by one.[12]

4. NON-CONVENTIONAL SYNTHETIC METHODS

The unconventional heating techniques, mainly including microwave (MW) radiations[13] and ultrasound (US) radiations,[14] are becoming more and more popular, due to that which make huge contributions to reduce reaction times and chemical waste, maximize the efficient use of raw materials and improve

products yields and purity in preparation of ILs.[15] The other methods, electrochemical process[16] and extractive method,[17] play a key role in preparation ionic liquids of high purity (up to 99.99%).

4-1. Microwave-Assisted Synthesis of ILs

Microwave, falling in between infrared waves and radio frequencies on the spectrum, is a form of electromagnetic radiation with wavelengths ranging 1 mm to 1 m and frequencies between 0.3–300 GHz.[18] Microwave heating, also called dielectric heating, results in energy transferring from microwave to the substance through two fundamental mechanisms: dipole rotation and ionic conduction. Dipole rotation is a process, in which polar molecules (dipoles or ions) possessing a dipole moment interact with each other. The dipoles or ions of the sample try to align themselves in the direction of the applying rapidly changing electric field when exposed to microwave irradiation. Ionic conduction refers to the instantaneous localized superheating of the ionic materials due to the charged particles motion generated by the oscillating electric field.[19]

A large body of evidence suggests that microwave-assisted synthetic method for ILs has a lot of unusual merits, compared with common heating method, such as shorter reaction time, higher product yields, non-contact heating, energy saving, higher selectivity and heating rates.[20]

The first study about microwave-assisted organic synthesis was performed in 1986 by Gedye et al.,[21] and from then on, this technique has been widely applied in chemical reactions as an environmentally friendly process.[22] In 2001, Varma et al. reported the neat preparation (open vessel) of several imidazolium-based ILs using unmodified household microwave oven under solvent-free conditions for the first time. The ILs were obtained in less than 2 min with yields higher than 70%.[23] In the same year, his group synthesized a series of ILs by combining 1-methylimidazole with alkyl halides in open vessel using the similar approach. The study showed that the production rate could be as high as 90% in less than 1 min.[24] Subsequently, based on the previous method, they synthesized another class of IL, 1,3-dialkylimidazolium tetrafluoroborates in 2002.[25] In 2005, the same authors improved the preparation of an imidazolium-based organogallate ([Bmim][$GaCl_4$]) using MW system under solvent-free conditions. What is more, the obtained ILs were used as active catalysts for acetal formation.[26]

Obviously, this method has not only efficiently reduced reaction time but also effectively avoided using excess of alkyl halides and organic solvents. However, every coin has two sides. Domestic microwave ovens fail to availably control reaction conditions, for example, continuous MW heating may result in formation of colored products.[27] It is hard to overcome the energy distribution during the reaction progress. To some extent, the reaction of alkyl halides in an open vessel is hazardous and the open vessel is not in favor of synthesizing hygroscopic compounds.[28] The disadvantages of this approach bring serious limitation in mass production.

From the perspective of domestic microwave system, time and irradiation power are the only changeable

parameters in organic synthesis. However, the real-time measurement of pressure and temperature is badly needed to solve.[29] In the last few years, with the endless development of new techniques, several microwave instruments were especially designed for organic synthesis, including multi-mode microwave and mono-mode microwave.[30] Such instruments, with microwave directly focused on the target reactor, could perform accurate on-line monitoring of temperature, power and pressure, in this way, which have been widely applied for producing ILs.[31]

Multi-mode microwave is well known for its universal applicability, controllable operation system, the existence of large cavity and wide output power.[32] Therefore, in 2002, Rebeiro et al. reported the synthesis of various ILs precursors in a large scale under professional multi-mode oven (CEM MARS-S) in a closed vessel.[33] Indeed, application of the modified microwave digester provided a simple and quick method to prepare ILs and greatly improved the procedure to meet the rules of "Green Chemistry". Deetlef et al. took a step forward to obtain ionic liquids-based imidazolium, pyrazolium and thiazolium with highly purity by utilizing an extremely small molar excess of haloalkane (1–2%). It is crucial for this method to avoid the use of massive solvents for purification.[34] Unfortunately, there still exist some disadvantages. Such as low energy efficiency, high operating temperature, non-linear radio frequency, heterogeneous distribution of microwave power, and so on.[35]

In order to make full use of microwave energy, dedicated equipment with mono-mode, also called single-mode cavities (CEM Discover), has become available and provided considerable advantages over multi-mode systems.[29] The single-mode cavities that own all kinds of reaction vessels provide a completely safe, independent system for organic preparations under the condition of relatively high frequency and elevated pressure.[36] Synthesis process is carried out at relatively low temperature with continuously stable input energy by using in situ cooling system (active cooling system), consequently the product rates increased vastly.[22,37] The Discover System dramatically accelerates automated operation by adding the Explorer module, thereby continual reactions could run in optimizing conditions.[38] The most important technology, the use of continuous flow module, not only help to easily completes scaling-up reactions but also achieve rapid on-line analysis.[38,39]

Due to these apparently controllable features, MW Reactor, as an efficient, convenient, alternative as well as harmonious applicator, attaches more and more importance to reaction engineering under region selective conditions, especially in ILs synthesis.[40] Recent studies described large amounts of rapidly synthesized second generation ionic liquids using the controllable single-mode microwave reactor. For example, two categories of novel ILs based on imidazolium and pyridinium cations were prepared with higher yields and shorter reaction time by Ibrahim et al.[41] In a similar study, Messali produced four new functionalized *N*-alkylpyridazinium ILs.[42] Thöming et al. obtained 1-butyl-3-methylimidazolium bromide with high purity on a large scale through utilizing a modified micro-reactor, which equipped with a

continuous operating system and a microstructured mixer, under solvent-free condition.[43]

Single-mode MW irradiation, as a clean, friendly, efficient system, has attracted widely attentions, some chemists even started to prepare chiral ILs from chiral precursors and explore the application in the area of a symmetric synthesis and organocatalysis.[44] In 2003, Thanh et al. firstly synthesized chiral ILs bearing ephedrinium cations under Focused Microwave activation in both closed and open vessels without any solvent.[45] Shortly afterwards, some scientists invented an effective microstructured reactor (MSR) with microfluidic devices.[46] Such microreactor usually is composed with multiple parallel channels in millimeter range, which provide high specific surface areas and allow for highly efficient heat exchanging,[47] micromixers, which reduce the mixing time and provide rapid mass transportation of reactions,[48] micro-channel heat exchanger, which attaches with high heat-transfer coefficient, provides homogeneous energy, avoids appearance of hot-spots and facilitates exothermic reactions,[49] and the continuous-flow devices, which could improve productivity as well as thermal management during synthetic processes.[50] As a result, desired products are of high quality, selectivity and yields under safe and controlled conditions.

These various modules of MRSs give new drive for ILs development in large scale and high purity at low energy consumption.[51] A kind of ILs, ethylmethylimidazole ethyl sulfate ([EMIM][$EtSO_4$] was synthesized in the MSR via alkylation of methylimidazole with diethyl sulfate under solvent-free conditions.[52] Zimmermann and his group obtained 1,3-dialkylimidazolium-based ILs under modified continuous Radziszewski reaction in a MSR. The synthesis started from available and relatively cheap precursors-monoalkylamines, glyoxal, formaldehyde, and mineral or organic acids within microwave activation.[53,54] The influence of various parameters has been discussed in order to improve production yields. Experimental results demonstrated that IL 1,3-dialkylimidazolium could be prepared continuously in high yields (70–90%). Compared with ILs synthesized in conventional method, the purities (>95%) were tremendously enhanced.

4-2. Ultrasonic-Assisted Synthesis of ILs

Not similar to rapid and dielectric heating of microwave irradiation, another new way to obtain ILs is ultrasound irradiation interacted with physical phenomenon, which has been used for many years in the field of organic synthesis.[55]

Sonochemistry ultrasound (US) devices operate with sound wave in frequencies from 20 KHz up to several gigahertzes, in wavelength from 10 to 0.01 cm. In general, the range of frequencies between 20–40 KHz are employed in chemical reactions.[55b,56] The power of ultrasound is not completely absorbed by single molecule; partial energy is transformed into heat.[57] US are brought out through the process of acoustic cavitations: involving the formation, growth and collapse of micrometer-sized bubbles in pure phase.[58] When acoustic waves propagate in the homogenous medium, vibrations of molecules generate

alternative compressions and rarefactions.[59] After the large negative pressure acts on liquids, small cavities or micro bubbles form, which expand and finally, collapse violently and release intense heat.[60] These localized high velocity collisions between particles create high temperatures (roughly up to 5000 °C) and pressures (about 1000 atm) in extremely short duration.[61]

Due to low level of waste, simplified manipulation and reduced energy consumption, the ultrasound becomes one of the promising synthetic techniques that are widely employed in ILs preparation.[62] Varma's group proposed in 2002 the use of US to synthesis of ILs.[63] In the first case, 1-alkyl-3-methylimidazolium halides and dialkyl-3-methylimidazolium dihalides were efficiently prepared at room temperature, under solvent-free conditions. This kind of reaction got better yield in shorter time, compared with conventional heating method.

Lévêque et al. put forward an ultrasonic-assisted method for the anion metathesis to prepare several 1-butyl-3-methylimidazolium salts (BF_4^-, PF_6^-, $CF_3SO_3^-$, etc.).[64] The reaction times were reduced from 30 h to 1 h with yields up to 90%. Later, their group also described an efficient one-pot synthesis of second-generation ILs, combining anion metathesis.[65] The work was carried out in a closed vessel under different conditions (simultaneous US/MW and US), a series of ILs with 1-methylimidazole cores were obtained in high yields (80–97%) after a period of time. The results demonstrated that the method with the use of sequential MW/US flow reactors had access to a wide range of ILs in short times, compared to US irradiation.

Messali and Asiri described the synthesis and characterization of two new ionic liquids derivatives for the first time, which are 1-benzyl-3-(4-phenoxybutyl)-1*H*-imidazol-3-ium bromide and 1-benzyl-3-(4-phenoxybutyl)-1*H*-imidazol-3-ium tetrafluoroborate, under the condition of ultrasound-assisted in short reaction time and with good yields.[66] In 2015, five new functionalized 1-alkyl-3-butylimidazolium ILs were prepared in a closed vessel by Messali et al. via an efficient green ultrasound-assisted procedure.[67] He was interested in the design and synthesis of a new series of functionalized ILs based on 4-(dimethylamino)pyridinium derivatives under ultrasound irradiation.[68] In 2015, continuing to his previous work, Messali successfully carried out 34 new, environmentally friendly picolinium-based ionic liquids via the identical approach with improvements in rate and yield of reactions.[69]

Figure 2 presents an overview of some possibilities based on the above-mentioned four cations, with the alky group.

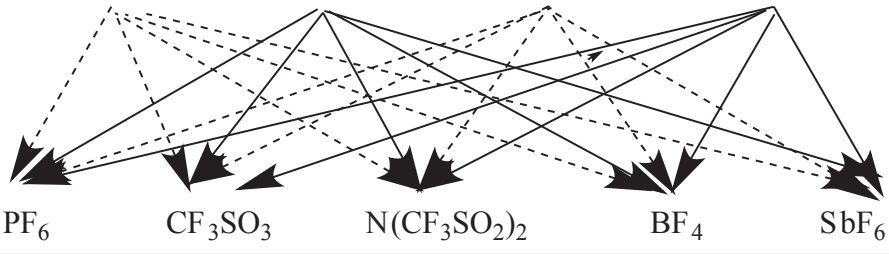
Chemical formula				
Cation's name	1-alkyl-3-alkyl-imidazolium	*N*-alkyl-pyridinium	*N*-alkyl-pyridazinium	*N*-methyl-*N*-alkyl-pyrrolidinium
Counter anions of first-generation ILs	chloride	bromide	bromide	chloride
Possible Counter anions of second-generation ILs				

Figure 2. Possible combinations for preparation of ILs through ultrasound irradiation

All the possible combinations presented in Figure 2 highlight a general ultrasound-based method to access to a variety of ILs, authorizing a very large panel of cations and/or the anions. As a final comment, we would like to emphasize that not only ILs based on imidazoliumcan be prepared, but also for ILs based on pyridinium, pyridazinium and pyrrolidinium. In this way, the range of possibilities of synthesized ionic liquids spreads through this method.

Compared with classical methods of synthesis, US-based techniques are proved to be more efficient because of the high speed, low amount of solvent or solvent-free conditions and the applicability to broaden spectrum of nitrogen based precursors. However, as discussed above, when ILs are exposed to US, the coloration and slight decomposition sometimes observed in the process of synthesizing are issues that need to be considered.[70] Thus the main challenge for the ultrasound-assisted synthesis of ILs could be scale-up, taking into account both the issues relating to sonochemistry and the slight degradation of the ILs under US.

4-3. Electrochemical Synthesis of ILs

In order to decrease the waste produced in traditional synthesis process and obtain more pure ILs without incomplete reactions and solvent contamination, an efficient method, the electrochemical process, is demonstrated to meet all of the requirements.

Generally, an electrochemical cell comprises a means for dividing the cell into two or more compartments.

These compartments include a catholyte compartment which houses a cathode and a catholyte solution and an anolyte compartment which houses an anode and an anolyte solution. In addition, the dividing membranes, including cation-exchange membranes, anion exchange membranes and bipolar membranes, are important comportments in this system.[71] The electrochemical cell is charged with at least two solutions, which compromise the desired ions (cation or anion) of the ionic liquid to be produced or that when subjected to electrolysis produces the desired ions. Undesired ions also would be produced during the process of electrolysis, and finally are converted to a gaseous by-product such as hydrogen, ammonia, carbon dioxide, or nitrogen, which are separated from the solution.[16] Consequently, obtained ILs achieved high purity with less undesired ions.

Hale et al. described a process that improved the purity of ILs by the electrolysis of the corresponding desired cation. What is more, the aqueous solution captaining ILs was heated to an elevated temperature for prolonged time before treatment in electrolysis cell. Consequently, obtained ILs efficiently reduced the halide content of ILs, with purity up to 99.99%.[72]

The other few investigators have also described preparations of extremely high pure ILs using electrochemical method. However, it is not suitable for the industrial productions due to the complex device and operating system used in this method. What's more, the problem of toxic gas produced during electrolytic progress is urgent to be solved.

4-4. Microwave-Assisted Synthesis of ILs

As mentioned above, another efficient method to produce colorless, high pure ILs that free of impurities is liquid-liquid extraction, which was exploited by General Electric Company.[17] Generally, ILs containing non-halide anions are prepared by performing an anion exchange reaction through extraction with an organic solvent composed of an aqueous solution an alkali metal salt of the anion and a corresponding quaternary halide.[73]

In 2009, Burrell et al. summarized synthesis of some kinds] of ILs-based on imidazolium and pyrrolidinum with different anions, such as Cl^-, BF_4^-, $[CF_3SO_3]^-$, etc.[74] At first, generated ionic liquid precursors were purified using a purification agent comprised of activated carbon or charcoal, subsequently, the purified ionic liquid precursors were used to prepare high pure and colorless ILs through the progress of continuous extraction and filtering impurities.

To some extent, this method does not be widely applied for synthesis of high pure ILs because of its certain restrictions, such as complexly operating, largely using organic reagents, etc.

5. CONCLUSION

In conclusion, we summarized some features of present approaches to produce ILs. These synthetic methods included traditional heating reflux, microwave irradiation, ultrasound irradiation,

electrochemical synthesis and extractive synthesis. At the same time, the advantages and disadvantages of different methods were compared. For example, it is better to choose microwave or ultrasound irradiation if you want to synthesize a certain IL with shorter reaction time and better yields. In doing so, we aim to help the corporations or individuals to search for the most suitable methods and lay the foundation for exploiting more ideal methods to provide high purity and better yields of ionic liquids in the future.

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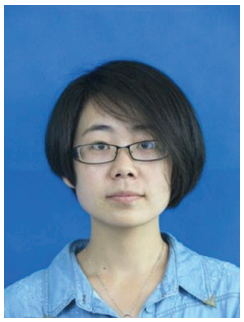

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