Ionic Liquids and Ultrasound in Combination: Synergies and Challenges

Journal:	*Chemical Society Reviews*
Manuscript ID:	CS-REV-06-2014-000193.R1
Article Type:	Review Article
Date Submitted by the Author:	18-Aug-2014
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Ionic Liquids and Ultrasound in Combination: Synergies and Challenges

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Abstract:

Ionic liquids, as reaction media, and sonochemistry are two recently developing fields of chemistry that present some similarities. Firstly, they constitute separately unconventional approaches to reaction chemistry that, in many cases, generate improvements in yield, rate and selectivity compared to classical chemistry, or even change the mechanisms or products expected. In addition, both are often associated with green chemistry concepts as a result of their properties and their possible eco-friendly uses. A recent trend has been to combine these two technologies in a range of different applications and the results demonstrate very significant and occasionally surprising synergetic effects. Here we critically review the advantages and limitations of the ionic liquid/ultrasound combination in different applications in chemistry, to understand how, and in which respects, it could become an essential tool of sustainable chemistry in the future. Many practical and theoretical aspects associated with this combination of techniques are not understood or resolved and we discus where fundamental studies might further advance this field.

1. Introduction

Ionic liquid media (abbreviated "ILs"), as well as sonochemistry (use of ultrasound in chemical processes, denoted "US", or as "))))" in schemes), are two recently developing technologies used in different fields of chemistry. Often, their uses in a reaction or process produce improvements in terms of efficiency, selectivity, yield, reaction time, recycling, and/or, in some cases, other unexpected results. The idea of combining these two efficient technologies was innovative and produced clear synergies in some cases, but it is important to look closely at the literature to understand how this unique combination can be optimized as a highly effect approach to a number of chemical processes.

In the last two decades, the use of ILs as reaction media reported in different areas of chemistry has increased considerably.[1,2] These solvents, commonly defined as a class of salts with low melting points (typically less than 100 °C)[3] or no melting point, have attracted intense attention from chemists. ILs present some unique properties often unavailable with traditional solvents, including, in various cases, negligible vapor pressure, high chemical and electrochemical stabilities, high polarity, etc.[3,4,5,6] Their application as reaction media is an area of very active research, and new approaches involving ILs have been proposed for aspects of energy chemistry,[7] preparation of materials,[8] biomass valorization,[9] analytical chemistry,[10] microextraction,[11] organic and pharmaceutical chemistry,[12] electrochemistry[13] and many others. Interestingly, Seddon has estimated that there are nearly one million simple ILs that can be easily prepared in the laboratory, leading to 10^{18} or more possible ILs if multi-ionic systems are considered.[14] As their physico-chemical, thermal and solvent properties are directly associated with the nature of the ions and their interactions, we can imagine as many applications or uses as there are different ILs. This represents a great advantage in terms of tunability for these solvents, but also a limiting drawback in term of the lack of theoretical and fundamental data about their properties to guide their use.

For its part, ultrasound-promoted synthesis has also attracted much attention during the past few decades.[15] The effects of ultrasound are the consequence of the cavitation phenomenon, i.e., the formation, growth, and collapse of gaseous microbubbles in the liquid phase.[16] The intense local effects (mechanical, thermal and chemical) due to the sudden collapse of these bubbles of up to a few micrometers diameter, are at the origin of all of the applications of sonochemistry.[17] By imploding, these bubbles create locally high pressures (up to 1000 bar) and temperatures (up to 5000 K) that can lead to high-energy radical mechanisms and also generate some interesting physical effects.[18] Many factors can affect the cavitation: the frequency, the acoustic power, the gas atmosphere, the hydrostatic pressure, the nature and the temperature of the solvent, the geometry of the reactor, etc.[19] The design of organic reactions under ultrasound requires a rigorous methodology and the complete report of all sonochemical parameters and experimental details. In the absence of these, it can be very difficult to reproduce an experiment from the literature.[20] Conditions obtained in a medium submitted to ultrasound can produce a number of physico-chemical effects, such as increased reaction kinetics, changes in reaction mechanisms, emulsification effects, crystallization, erosion, precipitation, etc.[21] To date, the major limitation to a thorough understanding of sonochemical phenomena is the lack of reported data relating to sonochemical parameters.[20]

To better understand how the IL/US combination has developed recently, we studied publications reporting the combined use of these two technologies (Figure 1). Of the approximately 600 peer-reviewed publications identified, about 79% are about applications in chemistry and the remaining 21% dealt with ultrasonic velocity in ILs (Figure 1a). In fact, the speed of ultrasound propagation represents a very much studied physico-chemical property, leading to the determination of reliable values for the adiabatic compressibility of ILs.[22] Knowledge of a thermodynamic property such as the compressibility is essential for the proper design of US-based industrial processes.[23] These measurements were also performed on mixtures of ILs with organic solvents (and also ternary mixtures with water) to study the nature of intermolecular forces in these kinds of liquid mixtures.[24] However, determination of ultrasonic speeds in ILs is not in the scope of this review and the associated publications have not been considered here.

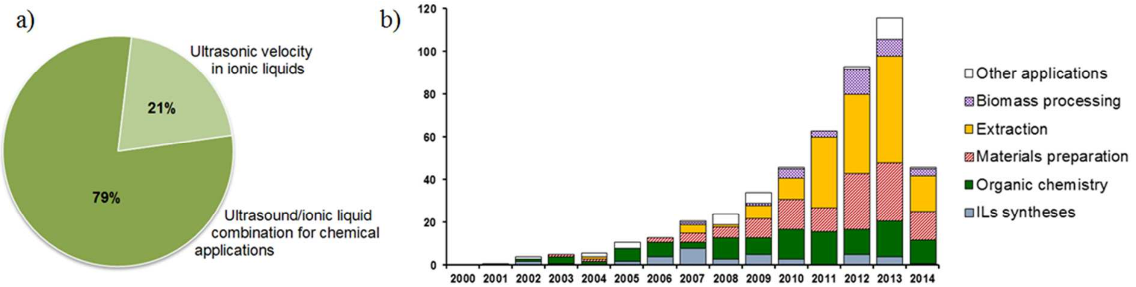


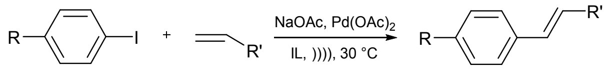
Figure 1: a) Distribution of all the publications found for "ionic liquids and ultrasound" SciFinder® search; b) Evolution of publications found for "ionic liquids and ultrasound" SciFinder® search, classified by applications and by year. (Data of June, 2014)

We focus here on the applications, and their potential, in chemistry of the IL/sonochemistry combination. Figure 1b shows the evolution of reported publications, year by year since 2000, as a function of the applications involving the IL/US combination: (1) use of US for the synthesis of ILs; (2) synergetic effects found in organic chemistry; (3) for materials preparation (catalysts, nanoparticles, nanotubes, etc); (4) for extraction and micro-extraction; (5) for biomass processing such as pretreatment of lignocellulosic feedstocks; and (6) others applications (electrochemistry, sonochemical degradation of ILs, etc).

The first example of this combination was reported by Srinivasan *et al.* in 2001 to promote C–C bond formation *via* an Heck reaction under ambient conditions and ultrasound (ultrasonic cleaning bath, 50 kHz) in 1,3-di-*n*-butylimidazolium bromide ($[C_4C_4im]Br$) and 1,3-di-*n*-butylimidazolium tetrafluoroborate ($[C_4C_4im][BF_4]$).[25] The ultrasound assisted Heck reaction of the iodobenzenes with alkenes at 30 °C showed complete conversion in just 1.5–3 h to afford the desired products in excellent isolated yields (73–87%, Table 1). No reaction under similar ultrasonic conditions was observed when the ILs were replaced by molecular solvents such as DMF and NMP and no reaction, even in traces, was observed under ambient conditions in the absence of ultrasound. Here there is a clear, combined effect, confirming that both IL and US are required for the reaction. In addition, under these conditions, the reaction rates were considerably enhanced and reaction times decreased, compared to the classical conditions. The authors demonstrated *via* NMR/MS and *in situ* TEM analyses the formation of a Pd-biscarben complex and its subsequent sonolytic conversion to a highly stabilized cluster of zero-valent Pd nanoparticles; this suggested that the enhancement in rate and yields were, at least in part, due to the formation of a new, highly active catalytic species. Following this dramatic example, many reactions have been tested during the last decade, under ultrasound and using ILs as solvents. The main results are discussed in section 2 of this review.

At a fundamental level, a further objective of this review is to explore how ultrasonic irradiation of non-volatile ILs affects the cavitation phenomenon in this medium, and investigate if the cavitation model of US can be directly applied to ILs. These mechanistic aspects of US action in ILs are discussed in section 2.2 of this review.

Table 1: Heck reaction of iodobenzenes with activated alkenes under sonication in $[C_4C_4im]Br/[C_4C_4im][BF_4]$ ILs.[25]



Entry	R	R'	Time under US (h)	Isolated Yield (%)
1	–H	–COOMe	2.0	81
2	–H	–COOEt	1.5	87
3	–H	–Ph	1.5	82
4	–OMe	–COOMe	3.0	82
5	–OMe	–COOEt	3.0	79
6	–OMe	–Ph	3.0	80
7	–Cl	–COOMe	1.5	79
8	–Cl	–COOEt	1.5	77
9	–Cl	–Ph	1.5	73

In 2002, Varma's and Lévêque's groups proposed around the same time the use of US to improve the synthesis of ILs.[26,27] The first group developed a solvent-free sonochemical protocol for the preparation of some 1-alkyl-3-methylimidazolium halides ILs, comparing both the use of an ultrasonic bath (40 kHz, 320–881 W), with a probe system (20 kHz, 750 W) and oil bath conditions.[26] From chloro-, bromo- and iodoalkanes and methylimidazole, excellent yields (mainly up to 92%) were obtained in substantially reduced times (from 25–34 h in "silent conditions", *i.e. without ultrasound*, to 0.5–2 h under ultrasonic irradiation). In addition, some dicationic ILs were also synthesized *via* this procedure.[26] Lévêque *et al.* reported the ultrasound-assisted preparation of several 1-butyl-3-methylimidazolium salts (BF_4^-, PF_6^-, $CF_3SO_3^-$ and BPh_4^-).[27] While the maximal isolated yield (80–90%) was reached after 30 h in silent conditions at room temperature, only 1 h is necessary to reach these results under ultrasound (20–24 °C maintained by a cooling bath, 30 kHz). The authors concluded that ultrasonic irradiation enhanced the anion exchange in the preparation of second generation ILs (the metathesis step). As discussed further in section 3, these two groups and others continued to propose improvements in the synthesis of ILs *via* ultrasonic processes.

The IL/US combination has increasingly been developed for preparation of materials (catalysts, nanoparticles, nanotubes, etc), extraction and micro-extraction processes, and biomass processing. These points are analyzed in section 4 of this review.

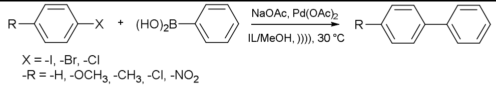
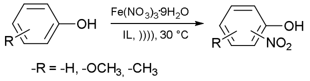
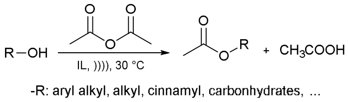
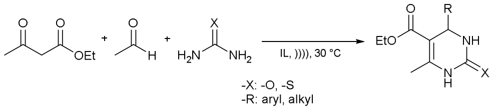
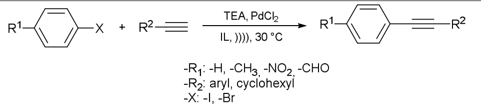
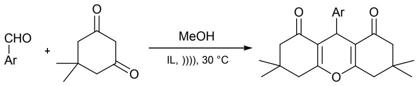
Thus, from the 2000s onwards, interest in the combined use of ILs and US has exponentially increased (Figure 1b). In this review, we critically review the advantages and the limitations of the IL/US combination in different applications of chemistry and identify the most promising avenues for development in the future.

2. Ionic liquid based ultrasound processes in organic chemistry

2.1. Synergetic effects observed in organic chemistry

As discussed above, the first examples of synergistic combinations of ILs and US involved C–C bond formation *via* a Heck reaction at ambient conditions.[25] From this example, the same research group studied other organic reactions such as Suzuki cross-coupling,[28] the nitration of phenols,[29] the acetylation of alcohols,[30] the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones,[31] the Sonogashira reaction,[32] and the synthesis of 1,8-dioxo-octahydro-xanthene derivatives.[33] Interestingly, as all of these experiments were performed by the same research group, the ultrasonic conditions are similar (cleaning bath, 50 kHz, same acoustic power), thus the results and effects involved by ultrasound are comparable (Table 2). In addition, the authors systematically compared their results to those under silent conditions during several hours in the IL medium and under sonication in molecular solvents such as acetonitrile, methanol, ethanol, THF, DMSO, hexadecane, PEG-400 and/or dichloromethane.

Table 2: Applications of IL/US combination reported by Srinivasan *et al.*

Entry	Reaction	IL	Experimental conditions	Sonochemical conditions	Results	Ref.
1		[C_4C_4im][BF_4]	MeOH as co-solvent, 30 °C, 20 to 90 min	Thermostated ultrasonic cleaning bath, 50 kHz	85–83 % (X = I); 82-85% (X = Br); 42–52% (X= Cl).	28
2		[$EtNH_3$][NO_3]	29–30 °C, 45 min	Thermostated ultrasonic cleaning bath, 50 kHz, 120 W (output power)	100% conversion; selectivity of 71-85% for *para* isomers.	29
3		[C_4C_4im]Cl, [C_4C_4im]Br, [C_4C_4im][ClO_4], [C_4C_4im][BF_4], [C_4C_4im][PF_6].	30 °C, 5 to 30 min	Thermostated ultrasonic cleaning bath, 50 kHz, 120 W (output power)	80–95% isolated yields.	30
4		[C_4C_4im]Cl, [C_4C_4im]Br, [C_4C_4im][ClO_4], [C_4C_4im][BF_4], [C_4C_4im][PF_6], [C_4im][BF_4].	30 °C, 30 to 70 min	Thermostated ultrasonic cleaning bath, 50 kHz, 120 W (output power)	64 - 97% isolated yields.	31
5		[C_4C_4im][BF_4]	30 °C, 2–3 h	Thermostated ultrasonic cleaning bath, 50 kHz, 120 W (output power)	68 – 93 % isolated yields.	32
6		[C_6C_4im][BF_4]	MeOH as co-solvent, 30 °C, 30 to 90 min	Thermostated ultrasonic cleaning bath, 50 kHz, 120 W (output power)	75–95 % isolated yields.	33

For the Suzuki coupling reaction under ultrasonic conditions in [C_4C_4im][BF_4], even the normally less or non-reactive chlorobenzenes showed significant conversions (~50 %; Table 2, entry 1).[28] For example, the coupling reaction of iodobenzene with phenylboronic acid performed at 30 °C in the absence of ultrasound showed only 25% conversion even after 10 h *vs*. 92% after 20 min under US. The authors once again demonstrated the acceleration of the formation of the Pd-biscarbene complex (Figure 2) from interaction of the Pd and the $C_4C_4im^+$ cation and the subsequent *in situ* generation of a zero-valent Pd-species as the active catalyst. In their sonicated Sonogashira reaction using $PdCl_2$ as catalyst and triethylamine as base (Table 2, entry 5),[32] they highlighted the formation of stable, well dispersed, spherical and highly crystalline Pd(0) nanoparticles under sonochemical conditions *via* TEM measurements. In acetone as solvent and under ultrasound, the nanoparticles were polydispersed and presented irregular morphology and diameter. Moreover, in a blank experiment, Pd(0) nanoparticles prepared by ultrasound irradiation in IL and acetone, were tested in the reaction in silent conditions. The cross-coupled product was obtained in 36% and 38% yields in acetone and the IL, respectively, compared to the 75% and 85% yields obtained in the total sonochemical reaction. Indeed, US not only generated the Pd(0) nanoparticles but also promoted and enhanced the catalytic activity of this species in the catalytic cycle of the reaction. In addition, the recycling of the Pd(0) nanoparticles was performed 5 times with only ~9% loss after 5 runs.[32]

Some other examples reported the improvement in dispersion[16] and depassivation[34] of nanoparticles *via* sonochemical activation. The choice of the IL is also crucial. For example, the *O*-acetylation of alcohols that is high yielding in imidazolium based ILs (Table 2, entry 3) in the absence of any catalyst was tested in other types of ILs such as ethylammonium nitrate and 1-*n*-bytylpyridium tetrafluoroborate; the reaction did not proceed beyond 50% conversion even after several hours of sonication.[30] The authors showed that hydrogen bond (Lewis/Bronsted acid) interaction of the C2-hydrogen of the imidazolium cation with the oxygen of the acetic anhydride was essential in the mechanism of the reaction. Under ultrasonic conditions, the reaction time decreased compared to silent conditions (4 to 12 times shorter). The synergistic role of the IL was confirmed by the fact that there was no reaction after several hours in a series of molecular solvents under ultrasonic irradiation.

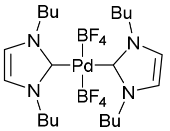


Figure 2: Pd-biscarbene complex proposed by Srinivasan *et al.*[28]

The combined use of US and ILs can also affect the selectivity of a reaction. For example, the nitration of phenols using $Fe(NO_3)_3$ was compared for both the same reaction time and the same conversion (Table 2, entry 2).[29] Thus, a high para-nitrophenol selectivity (85%) with 100% conversion was obtained under ultrasound after only 45 min in ethylammonium nitrate IL ($[EtNH_3][NO_3]$), while under silent conditions, only 74% selectivity was observed after 12 h (after 45 min, conversion was only 35%). In dioxan the conversion is total after 45 min under ultrasound and 5 h under silent conditions, with 73% and 60% selectivities, respectively. The authors proposed a mechanism that involves the homolytic cleavage of the initially formed phenol-Fe(III) complex leading to the formation of the phenoxy radicals, followed by the reaction with the NO_2 radicals generated by the splitting of the $(O_2N)Fe(III)–O–NO_2$ species. However, it is known that the chemical effects (and the radical formation) are more favored at high frequency than at low frequency (here, 50 kHz).[15,17]

Indeed, the frequency is an essential parameter; even if the whole mechanism is not elucidated yet, it is usually accepted that, in water, low frequencies (20 to 80 kHz) lead preferentially to cavitation induced physical effects (including shockwaves, microjets and erosion *via* asymmetric bubble collapse near the solid surface present, micro-convection, microemulsion formation, microstreaming, *(i.e.* a kind of liquid flow in a small region around the cavitation bubble).[15–16] On the contrary, high ultrasonic frequencies (150 to 2000 kHz) favor the production of hydroxyl radicals ($HO^\bullet$) through the local hotspots produced by cavitation, mainly leading to chemical effects. Thus, it is possible to identify two large regimes of power ultrasound applications in chemistry, based either on sonophysical effects or sonochemical effects.

In the case of non-volatile ILs, cavitation bubbles formed should contain essentially molecules of the solute only, leading to their preferential activation without the participation/interference of the solvent medium. For example, the lack of chemical involvement of the BF_4^- anion of $[C_6C_4im][BF_4]$ in any cavitational activation under US was confirmed through ^{19}F NMR, where no changes were observed.[31]This is one of the important aspects of the use of ILs as an US medium, which can force even less volatile substrates to undergo cavitational activation.

The same synergetic effects were widely reported by other research groups for many organic reactions such as Heck arylation,[35] Mizoroki-Heck reactions,[36] Suzuki aryl-aryl cross-coupling,[37] Knoevenagel condensation,[38] Morita-Baylis-Hillman reaction,[39] Sonogashira coupling reactions,[40] the synthesis of aryl azides,[41] the synthesis of 2,3-disubstituted benzo[*b*]furans,[42] Michael addition of 1,3-dicarbonyl compounds to nitroalkenes,[43] Kabachnik-Fields reactions,[44] and many others. Here, our goal is not to comment on all of the examples reported in the literature, but to identify the most important common features and mechanistic understanding. In all cases, similar advantages are described: significant reduction of reaction time compared to silent conditions, improvement in yields and selectivities, need of lower catalyst loading, decrease in the volume of solvent medium needed and ability to recycle the IL several times. As such these IL/US based processes offer significant advantages in terms of green chemistry.[45]

Interestingly, US irradiation was sometimes compared to microwave (MW) activation. Thus, US/IL and MW/US processes can be grouped, as non-conventional energy sources, in the same studies such as Diels-Alder reactions,[46] the Heck reaction,[47] the synthesis of lactones,[48] and other examples in organic chemistry.[15b,49] In fact, both of these approaches to activation often lead to the same effects on the reaction, mainly by reducing the reaction time.

Some examples also describe the IL/enzyme/ultrasound combination. Indeed, ILs were shown as good reaction media for biocatalysis, even if the reaction rates of enzymes are usually lower than those in conventional organic solvents.[50] The rate limitation is often caused by the low mass transfer rate due to the viscosity of ILs; this can be overcome by using US. For example, Lee *et al.* reported an enhancement of enzyme activity for the lipase-catalyzed transesterification of glucose in 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[C_4mim][TfO]$) under ultrasound (47 kHz, ultrasonic bath, 185 W).[51] Compared to the silent conditions, the same conversions were obtained 2.6 times more rapidly. Gumel *et al.* used ultrasonic irradiation for the lipase catalyzed synthesis of poly-6-hydroxyhexanoate via ring opening polymerization of ε-caprolactone in 1-ethyl-3-methylimidazolium hexafluorophosphate ($[C_2mim][PF_6]$).[52] In this case, US enhanced the rate of polymerization and the quality of the polymer produced (increase of its molecular weight and its crystallinity, reduction of its polydispersity). These effects were explained by the authors by the improvement in the mass transfer and the enhancement of the turnover number of the enzyme subjected to sonication-induced cavitation microstreaming.

Interestingly, the combination of US and ILs is also productive in the phase-transfer catalysis based synthesis of butyl salicylate[53] or mandelic acid.[54] For example, mandelic acid was prepared using 40–80 kHz ultrasonic irradiations (input power of 120 W) in $[C_4mim][PF_6]$ (99,8% purity), from benzaldehyde with chloroform in the presence of tetrabutyl ammonium bromide as a phase transfer catalyst.[54] In the absence of ultrasound, the reaction must be performed for 8 h to produce only 42% yield, while under 60 kHz ultrasound irradiation, the yield was 90% after 2 h. In addition, the phase transfer catalyst is essential to reduce the reaction time and increase the yields. It is likely, in this rather complex case, that the effects of the irradiation are manifest in both phases as well as at, or near, the phase boundary; it is possible that an additional effect of the ultrasound is to increase the dispersion of the phase transfer catalyst, increasing its surface area.

In previous studies, Chatel *et al.* showed the epoxidation of cyclohexene, cyclooctene, styrene and α-pinene with good yields in only 1 h in the presence of a manganese tetraphenylporphine and hydrogen peroxide, using the hydrophobic methyloctylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[C_8mpyr][NTf_2]$) under 20 kHz ultrasound irradiation.[55] The results suggested a switch of reaction mechanism according to the chosen experimental conditions: (a) acetonitrile/silent stirring or (b) IL/US activation. In the first case, the metalloporphyrin was quickly degraded and its recycling was not possible. In the optimized conditions (b), the IL prevents the degradation of the catalyst. Moreover, the reaction time was significantly reduced under US. In the latter conditions, the epoxidation reaction could occur *via* a classical high-valent oxo-manganese porphyrin complex. To unambiguously prove these mechanisms, a chiral Mn porphyrin complex was used as catalyst: in the classical conditions (a), the racemic mixture of epoxides was obtained while in the conditions (b), the ultrasonic asymmetric catalysis in IL clearly showed that the mechanism involves the metalloporphyrin catalyst route.[56] Thus, the IL/US combination improved the yields and decreased reaction times, but also involved a new reactivity for this epoxidation reaction.

In summary, it is clear that, in a wide range of organic reactions, the IL/US combination is often described in catalytic reactions as improving the yield, the selectivity and the global efficiency of the process. However, the origins (mechanical versus chemical) of these outcomes may be several-fold depending on the irradiation power and the nature of the reaction.[57] Thus it is important not to over-generalize on the impact of the IL/US combination. We note also that in some reports a valid comparison with classical conditions is not described and therefore the true impact of the IL/US combination is not clear; we commend all researchers studying these fascinating effects to provide a clear set of control experiments to provide a basis for unambiguous conclusions.

2.2. Effects of ultrasound irradiation on non-volatile ionic liquids

These studies lead us to question more fundamentally about the process occurring in ILs under irradiation. What are the effects of ultrasound on non-volatile ILs? In 2003, Suslick's group investigated the sonochemistry and sonoluminescence of some imidazolium based ILs $[C_4mim]Cl$, $[C_4mim][BF_4]$, $[C_4mim][PF_6]$ and decylmethylimidazolium tetraphenylborate $[C_{10}mim][BPh_4]$) under 20 kHz irradiation (60 $W.cm^{-2}$) for 3 h at 85 and 135 °C under an Ar flow.[58] During sonication, all the studied ILs darkened from colorless to amber, indicating some decomposition. The IR spectra, ^{13}C NMR spectra, ^{19}F spectra, fast atom bombardment mass spectra (FAB-MS), UV-visible spectra and elemental analysis of ILs contained no significant difference before and after sonication. However, the ^{1}H NMR spectrum obtained after sonication contained some additional peaks in the imidazole region amounting to 0.44% of total hydrogen. Interestingly, the headgas over each sonication was analyzed by GC-MS (Table 3). During sonication, the imidazolium based ILs produced gases containing traces of light hydrocarbons and nitriles, clearly due to the degradation of the imidazolium rings. Headgases from sonication of [C_4mim][BF_4] and [C_4mim][PF_6] contained no detectable fluoride-containing species and from [C_{10}mim][BPh_4] contained 72% benzene and traces of other cyclic products.

Table 3: Headgas composition during sonication of ILs[58]

Entry	IL	Headgas components
1	[C_4mim]Cl	chlorobutane (25.6%), chloromethane (51.1%), imidazole decomposition products (23.3%)[a]
2	[C_4mim][BF_4]	imidazole decomposition products [a]
3	[C_4mim][PF_6]	imidazole decomposition products [a]
4	[C_{10}mim][BPh_4]	Benzene (71.6%), toluene (7.8%), cyclopentadiene (1.4%), 1-hexene (0.5%), 2,4-hexadiene (0.7%), imidazole decomposition products (18%)[a]

[a] Imidazole decomposition products : 1,3-butadiene (0.4%), 1,3-butadiyne (2.2%), acetonitrile/isocyanomethane (21.9%), 2-methylpropane (60.7%), 2-propenenitrile (7.4%) and pent-3-en-1-yne (7.4%).

Suslick *et al.* also compared the multibubble sonoluminescence (MBSL) spectra of [C_4mim]Cl, 1-methylimidazole and 1-methylimidazole with 1.5% *n*-butyl chloride, showing molecular emission from excited states of C_2 carbon and CH (Figure 3). Like sonochemistry, sonoluminescence derives from acoustic cavitation, the implosive collapse of the bubbles, generating huge pulses of energy, which leads to the emission of photons.[59] They concluded from the products analyzed by ^{1}H NMR, that the headgases and the MBSL spectra are a result of the ultrasonic decomposition of both the ILs themselves and of their primary sonolysis products.[58,60] The primary decomposition products for the imidazolium based ILs are *N*-alkylimidazoles and 1-alkylhalides.

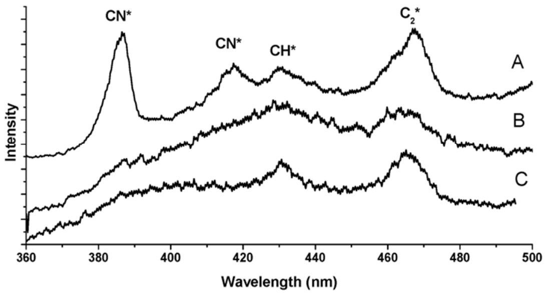


Figure 3: MBSL spectra of (A) 1-methylimidazole, (B) 1-methylimidazole with 1.5% *n*-butyl chloride and (C) [C_4mim]Cl. Reprinted with permission from Ref. 58 (Copyright 2014 American Chemical Society).

In another study, Chatel *et al.* showed that hydrophobic NTf_2-based ILs decomposed under 20 kHz ultrasonic irradiation and identified the corresponding degradation products.[61] In fact, even if the proportion of these degradation products were limited (~ a few ppm), it was sufficient to prevent the recycling and the reuse of ILs in an organic reaction. As a theoretical point, the sonoluminescence spectra confirmed that cavitation occurs in pyrrolidinium- (Figure 4) and piperidinium-based ILs, showing the usual sonoluminescence continuum and molecular emissions from excited states of CN and C_2.

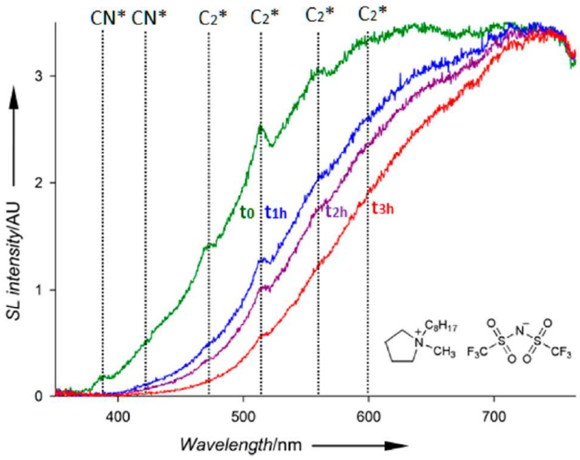


Figure 4: MBSL spectra [C_8mpyr][NTf_2]. Reprinted with permission from Ref. 61 (Copyright 2014 American Chemical Society).

The primary and secondary sonolysis products of [C_8mpyr][NTf_2] were identified *via* (1) the online detection of gaseous organic products in the headgas over the sonication, (2) the quantification of sulfur ions and (3) the analysis of volatile impurities trapped in the degraded IL due to headspace technology.[61] Interestingly, from this identification, the mechanisms of sonochemical degradation of [C_8mpyr][NTf_2] were determined to mainly involve pyrolysis reactions at the site of collapse of the cavitation bubbles. No product of oxidation by $HO^\bullet$ radicals was detected. Thus, analyses reported degradation products of the octyl chain (44%), benzene derivatives obtained through reforming mechanisms (20%), derivatives of acrylonitrile obtained from ammoxidation of propene under air (6%) and sulfur-containing compounds resulting from the degradation of the NTf_2^- anion (3%). The temperatures and pressures required for pyrolysis reactions fit with the intense local heating (about 5,000 K) established when cavitation bubbles collapse.

The results obtained in this study[61] and Suslick's works[58,60] are consistent with the two-site model of sonochemical reactions (Figure 5) involving the bubble's gas-phase interior and the immediately surrounding shell of liquid phase.[62] Ashokkumar *et al.* recently determined a temperature of about 3500 K generated in the imploding cavitation bubbles in 1-ethyl-3-methylimidazolium ethylsulfate ([C_2mim][$EtSO_4$]).[63] In addition, the authors observed an enhancement in the sonoluminescence intensity with increase in bulk fluid temperature corresponding to the decrease in viscosity of the IL (94 mPa.s at room temperature *vs.* 14.4 mPa.s at 80 °C), indicating an increasing rate of cavitation.

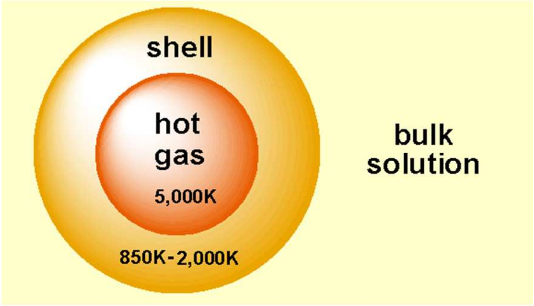


Figure 5: Two-site model of sonochemical reactivity.

To limit the degradation of hydrophobic ILs under ultrasonic irradiation, the system was shifted to a water/IL biphasic system.[61] The degradation products amounts were reduced by 20 times in a biphasic system since hot spots could occur preferentially in the aqueous phase rather in the IL, mainly due to the difference of viscosities and vapor pressures between these two media. This method allowed the oxidation of alkenes under US in the biphasic system, without the degradation of the IL, allowing its recycling.

In another study, Chatel *et al.* determined for the first time, the acoustic power when some NTf_2^-- based ILs are submitted to ultrasound to better understand the effects of US on ILs.[64] Despite very different specific heat capacities (c_p) for water and for ILs, the acoustic powers measured for the same electric power were very similar for both media. Thus, the faster heating up of the ionic liquids (due to lower heat capacity) compared with water can lead to interesting effects as a solvent for organic reactions (Figure 6).

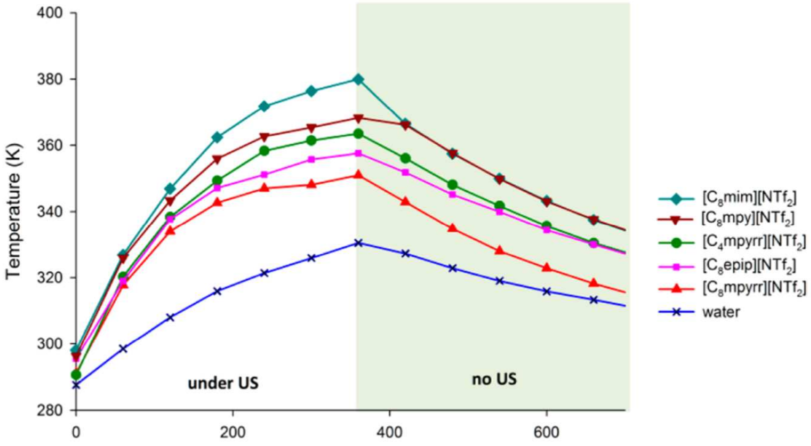


Figure 6: Temperature rise measured in some ILs and in water under US with P_{elec} = 11.5 W. Reprinted with permission from Ref. 64 (Copyright 2014 American Chemical Society).

These studies highlight an important issue – that IL degradation may be a significant process in the application of the IL/US combination to organic reactions and cannot be ignored. Potentially the IL will only be recyclable under carefully controlled conditions and these needs to identify by thorough identification of any breakdown products that appear. It is also important to recognize the possible role of these breakdown products in the enhancement of the chemical reactions taking place in the process. The potential degradation of ILs during sonication represents a real issue for the industrial applications of the IL/US combination. In addition, the recovery and recycling of the ILs may require the use of organic solvents and further energy input, raising the environmental impact of the process. Solutions should to some extent be able to be developed to deal with these issues through the appropriate choice of the nature of ILs and the careful optimization of the sonochemical parameters involved in each process.

Further investigations are needed to probe whether the cavitation model can be applied more broadly to all non-volatile ionic liquids. On the other hand, distinctly volatile, *protic* ILs, in which proton transfer to form the neutral acid and base compounds is possible, represent a completely different case in this context, and little is known about the effect of US on these ILs.

3. Green synthesis of ionic liquids under ultrasound

As mentioned in the introduction, Varma's and Lévêque's groups proposed in 2002 the use of US to provide an impressive improvement in the "green" aspects of the synthesis of ILs (Figures 7 and 8).[26,27] In the first case, 1-alkyl-3-methylimidazolium halides and dialkyl-3-methylimidazolium dihalides were efficiency prepared at close to room temperature, under solvent-free conditions (Figure 7).[26] The reaction times were reduced by 10–60 times with yields up to 90%, compared to reactions in an oil bath at temperatures reached under sonication conditions.

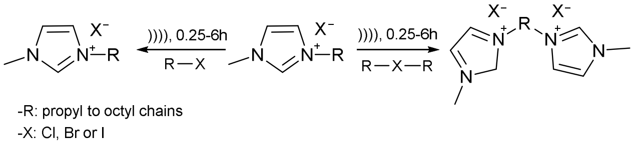


Figure 7: Ultrasound-assisted preparation of 1-alkyl-3-methylimidazolium halides proposed by Varma *et al.* (US: 20 kHz, ultrasonic bath and probe system)[26]

Lévêque *et al.* proposed an ultrasonic-assisted method for the metathesis step from 1-butyl-3-methylimidazolium chloride to associated common weakly coordinating anions such as BF_4^-, PF_6^- or $CF_3SO_3^-$ (Figure 8).[27] The reaction times were reduced from 30 h to 1 h with yields up to 90%. The authors suggest that the solid phase particle size reduction effect explains the enhancement of this reaction under ultrasonic irradiation.

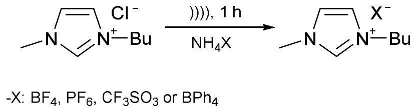


Figure 8: Ultrasound-assisted preparation of 1-alkyl-3-methylimidazolium salts proposed by Lévêque *et al.* (US: 30 kHz, probe system)[27]

A number of other reports including those of Varma,[65] Lévêque,[66,67] Zhao,[68] Cravotto,[66,69] Li[70] and more recently Messali,[71] describe sonication during IL syntheses that mainly leads to an important reduction of reaction time compared to classical methods. Some reviews have also discussed the use of low-frequency ultrasound or/and microwaves as activation methods for ILs syntheses.[72,73] Interestingly, Deetlefs and Seddon assessed the "green" credentials of the syntheses of ILs promoted by ultrasonic irradiation.[74] Indeed, the reduced preparation times induced by hotspots and small sized bubble formation, represent a significant green advantage compared to traditional methods, especially when the preparation is performed solvent-free. However, the authors noted that, as discussed above, the coloration and slight decomposition sometimes observed when ILs are exposed to US is an issue.[58,61] From an industrial point of view, this could be very limiting since the purification and decolorisation of the salts that is required as a consequence leads to poor *E*-factors. Thus the main challenge for the ultrasound-assisted synthesis of ILs could be scale-up, taking into account both the issues of relating to sonochemistry and the slight degradation of the ILs under US.

4. Application of IL/US in combination in other areas of chemistry

The objective of this section is not to review all of the examples of the use of the IL/US combination in the literature, but rather to highlight the essential advantages of the IL/US combination in recent applications, in particular in materials synthesis, electrochemical applications, extraction and micro-extraction and in lignocellulosic biomass dissolution.

4.1. Material synthesis

In the material synthesis area, the combined use of ILs and US was investigated in the synthesis of methanofullerene derivatives (Figure 9).[75,76] Indeed, unique chemical and physical properties of fullerenes can lead to important applications in medicine, optics and material science. Performed in [C_4mim][BF_4] instead of THF as solvent, the yield and reaction activity were improved *via* an increase of the dehalogenation reaction rate. However, the authors did not explore the role of the IL/US combination in the process. It is important to note that the 2–3 days under ultrasonic irradiations is not efficient in term of energy consumption, compared to magnetic stirring.

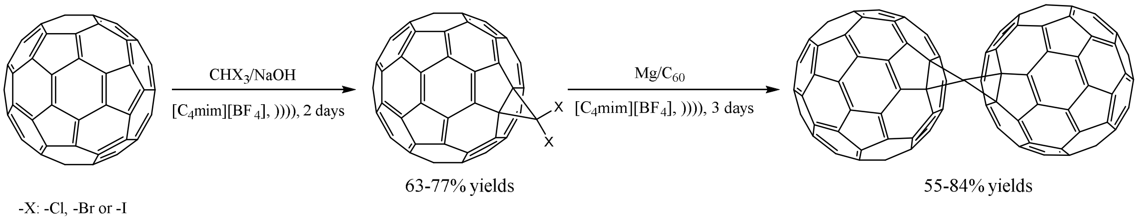


Figure 9: Ultrasound-assisted preparation of fullerenes in [C_4mim][BF_4][76]

The US/IL combination has also been used for graphene sheet preparation. For example, Dai *et al.* prepared a high concentration, stable graphene suspension in [C_4mim][NTf_2] (up to 0.95 mg.mL^{-1}) from a dispersion of graphite, under 20 kHz ultrasonic irradiation (60 min).[77] Shi and Zhu reported an IL-Pd-graphene nanocomposite prepared *via* a sonoeletrochemical route, as an efficient electrochemical sensor for chlorophenols.[78] In this case, the ILs played the role of a linker[79] and enhanced the catalytic activity. Sonication presents known effects on the synthesis and modification of grapheme, including the exfoliation of the graphite into discrete graphene sheets, suppressed aggregation in the reduction of graphite oxide compared to classical mechanical stirring and the promotion of the crystallization of nanoparticles by ultrasonic cavitation.[80] Liu *et al.* also reported the exfoliation of graphite into graphene sheets in 1-butyl-3-methylimidazolium cholate, and their stable dispersions that were achieved under 20 kHz ultrasonic irradiation.[81] They also applied this technique to achieve a Pd-nanoparticle-graphene hydrid, which was used as a catalyst for CO oxidation.[82]

Table 4: Examples of nanocrystal preparation in IL under US

Entry	Nanocrystal	Solvent	Ultrasonic conditions	Experimental conditions	Remarks	Ref
1	ZnS	$[C_4mim][BF_4]$/water	Ultrasonic cleaning bath, 120 W, 40 kHz.	30 min, rt	Stabilization effect, more defects on the particles'surface.	83
2	ZnS	$[C_2mim][EtSO_4]$/water	0.7 cm diameter Ti horn, 140 W, 23 kHz.	7 min, rt	Production yield is considerably higher compared to 20 h under mechanical stirring.	84
3	ZnO	$[C_6mim][NTf_2]$/water	Ti horn, 50 W (acoustic power), 40 kHz.	60 min, rt	No ZnO obtained without US, and without IL. Some active sites can be produced on some areas of ZnO nuclei surrounded by $[C_6mim]^+$.	85
3	ZnO	$[C_2mim][EtSO_4]$/water	0.7 cm diameter Ti horn, 140 W, 23 kHz.	60 min, rt	Short preparation time compared to classical method.	86
4	Sb_2S_3	$[C_4mim][BF_4]$/ethanol	Ultrasound bath, 70 W, 42 kHz.	24 h, 60 °C	Promotion of higher crystallization degrees.	87
5	SnS	$[C_4mim][BF_4]$/ethanol	0.3 cm diameter Ti horn, 100 W, 20 kHz.	10–60 min, rt	Formation of small nanoparticles.	88

Several preparations of nanocrystals such as ZnS, ZnO, Sb_2S_3 or SnS were performed in imidazolium based ILs, under 20–40 kHz US irradiation (Table 4).[83–88] The as-prepared nanocrystals were stabilized in the medium and ultrasonic treatment allowed a decrease of preparation time compared to classical treatments. In addition, the crystallization degrees were often higher and the particles were smaller. In the same way, IL/US was applied to the synthesis of nanorods (CuO,[89] ZnO,[90] MoO_3,[91]…) and nanotubes.[92,93] Ultrasound allowed the effective dispersion of carbon nanotubes but, as it can also damage them by cavitation,[94] it was shown that, once dispersed in an IL ($[C_4mim][BF_4]$), their integrity was maintained and aggregation prevented.[93]

Numerous papers have reported nanoparticle synthesis and stabilization in ILs,[95] and their sonochemical activation was observed in catalytic processes *via* dispersion improvement and surface depassivation.[96] Associating both technologies led to synergetic effects in many cases. For example, Jin *et al.* developed a sonochemical method for the preparation of gold nanoparticles capped by a thiol-functionalized IL using hydrogen peroxide as a reducing agent.[97] Here again, ultrasound (40 kHz, 80 W) accelerated the formation of gold nanoparticles and helped their dispersion in the IL. The function of the thiol groups in the selected IL was to prevent Au^0 particles from aggregating and the 1-(2',3'-dimercaptoacetoxypropyl)-3-methylimidazolium 3''-mercapto-1''-propanesulfonic acid IL controlled the subsequent growth of nanoparticles in the aqueous media, thanks to the thiol groups both in the cation and anion.[98] Behboudnia *et al.* applied their sonochemical preparation method in a 1-ethyl-3-methylimidazolium ethyl sulfate/water mixture for the synthesis of several nanoparticles such as SnO_2, CuS, PbS, CdS (Table 5, entries 1–4).[100–103] In all cases, the preparation was fast, efficient and led to very small and highly dispersed nanoparticles. Others examples have reported the same advantages in different ILs (Table 5).[99,104–106]

Table 5: Examples of nanoparticles preparation in IL under US

Entry	Nanoparticles	Solvent	Ultrasonic conditions	Experimental conditions	Remarks	Ref
1	SnO_2	$[C_2mim][EtSO_4]$/water	0.7 cm diameter Ti horn, 140 W, 23 kHz.	60 min, rt	Environmentally benign method. Fast preparation.	100
2	CuS	$[C_2mim][EtSO_4]$/water	0.7 cm diameter Ti horn, 140 W, 23 kHz.	7 min, rt	Highly monodispersive of spherical nanoclusters in comparison to classical preparation methods.	101
3	PbS	$[C_2mim][EtSO_4]$/water	0.7 cm diameter Ti horn, 140 W, 23 kHz.	7 min, rt	Short reaction time.	102
3	CdS	$[C_2mim][EtSO_4]$/water	0.7 cm diameter Ti horn, 140 W, 23 kHz.	60 min, rt	Preparation of very small size and pure crystalline CdS nanoparticles.	103
4	TiO_2	$[C_3\text{-OHmim}][NTf_2]$/water	Ultrasonic bath, 60 W, 45 kHz.	9 h, rt	Not need of calcination steps or addition of any templates or surfactants.	104
5	Ag	$[C_4mim][SbS_6]$, $[C_4mim][PF_6]$, $[C_4mim][NTf_2]$, $[C_4mim][OTf]$, $[C_4mim][BF_4]$, $[C_4mim]Cl$	Not indicated.	10–90 min, rt	Synthesis of Ag nanoparticles without using external reductants (hydrides, H_2, …)	105
6	Fe_2O_3	$[C_2mim][BF_4]$	Ultrasonic probe (100 mW), frequency not indicated.	90 min, 0 °C	Not need to use stabilizing or capping agents.	106

Interestingly, Wittmar and Ulbricht discussed the sonochemical dispersion of various titania nanoparticles in $[C_2mim][NTf_2]$ and $[C_2mim][BF_4]$.[107] Experimentally, they only used an ultrasonic bath (low frequency, 80 W), less powerful than a direct irradiation with a sonotrode to avoid IL decomposition. However, under these conditions, the forces induced by ultrasound did not break the strong bonds in the hard aggregates, leading to poor dispersions. Some examples have also reported the use of ultrasound in reactions involving nanoparticle supported ILs[108] or modified by ILs.[109] These ecofriendly methods generally result in easy workup, short reaction times, low waste production and high yields.

We can also mention the use of the IL/US combination for energetic materials preparation. For example, Anderson *et al.* applied low frequency ultrasonic irradiation on boron nanoparticles in 1-methyl-4-amino-1,2,4-triazolium dicyanamide and 1-butyl-3-methylimidazolium dicyanamide ILs,[110] known as hypergolic energetic ILs (EILs).[111] A capping layer was formed, however, that provided protection against oxidation that was better for the particles milled with the ILs, compared to the particles that were sonicated with the IL after milling.[110] In the view of the authors, the milling could drive more complete reaction, protecting the boron from oxidation during subsequent air exposure. However, we can note that in the "post-milling IL-capping" experiments the particles had substantial exposure to the glovebox atmosphere during the post-milling workup, while the particles milled with ILs are capped immediately as they form. In this case, it is difficult to make firm conclusion since the particles would be much less affected by possible oxidation by contaminants in the glovebox atmosphere. In the same way, Lv *et al.* developed an efficient synthesis of hexanitrohexaazaisowurtzitane using ILs and US.[112]

In conclusion, low frequency ultrasonic irradiations have been extensively used for the synthesis of materials in ILs, in particular to improve the dispersion of the particles. The main effect of this combination is the reduction of preparation times, and often, better quality of the synthesized materials.

4.2. Electrochemical processes

Electrochemical applications using ILs and assisted by ultrasound have also shown some advantages in the literature. For example, Fuchigami *et al.* worked on the electrochemical fluorination in fluoride and imidazolium based ILs under 45 kHz ultrasound irradiation *via* an immersible transducer positioned at the level of the anode during the electrolysis.[113,114] In these experimental conditions, they clearly showed the promotion of the mass transfer in the fluorination of ethyl α-phenylthioacetate, leading to increased yield and selectivity of the corresponding α-monofluorinated and α,α-difluorinated products, depending on the current passed. In addition, sonication changed the stereoselectivity of the anodic fluorination of 4-thiozolidinone.

Hardacre *et al.* compared the electroreduction of *N*-methylphthalimide to 3-hydroxy-2-methyl-isoindolin-1-one in ILs using phenol as a proton donor under silent and ultrasonic conditions (Figure 9).[115] In the presence of ultrasound (3 mm diameter titanium microtip, 25 kHz, 95 W.cm^{-2}), the rate of electroreduction increased and high currents were observed without affecting the selectivity for the reaction. However, some darkening of the IL phase was found to occur during the reaction and some anion decomposition was observed by the generation of fluoride under ultrasound using ion chromatography.[115] For the synthesis of imidazole-2-thiones, electrochemistry and sonochemistry were combined, but successively.[116] Indeed, the electrochemical reduction of 1,3-dialkylimidazolium ILs gave first the corresponding *N*-heterocyclic carbenes that, after reaction with elemental sulfur under ultrasound (22.5 kHz, 100 W), yielded 1,3-dialkylimidazole-2-thiones in very high yields in very short times.

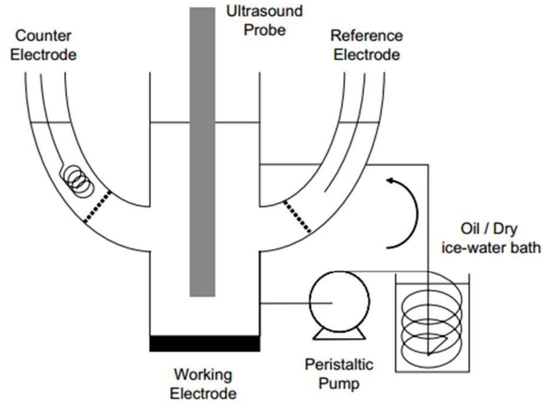


Figure 9: Electrolysis cell and heating/cooling system for the electroreduction of *N*-methylphthalimide in [C_2mim][NTf_2] under ultrasound. Reprinted with permission from Ref. 64 (Copyright 2014 Elsevier).

The anodic substitution reaction of *N*-(methoxycarbonyl)pyrrolidine with allyltrimethylsilane in [C_2mim][BF_4] involving ultrasound illustrated the advantages of operating in a single reactor, trapping the carbocations in sub-micrometre range nucleophile droplets formed by ultrasound irradiation (3.2 mm diameter horn, 20 kHz, 150 W.cm^{-2}).[117]

In a more general sense, low frequency ultrasound activation appears to improve electrochemical processes mainly *via* stirring effects (increase of mass-transfer coefficients),[118] continuous cleaning of the electrode surface and enhancement of reaction rates.[119] For these reasons, some examples of ultrasonic-electrodeposition processes in ILs were reported by Zeng's[120–123] and Zheng's[124] research groups.

4.3. Extraction and micro-extraction

As we presented in Figure 1b in the introduction of this review, the most important contribution of the IL/US combination is now in the extraction area; in 2013, 40% of the publications. Here, we do not present all of the examples from the literature, since the technology is very similar in all cases, but instead try to probe the reasons for the synergistic properties in this context. In fact, ILs and US are widely used, separately, extraction processes. Sometimes heat-reflux extraction is laborious, time consuming and requires large amounts of volatile and hazardous organic solvents. Ultrasonic-assisted extraction of organic compounds directly from matrixes demonstrates several benefits such as reducing processing time and energy, efficiency in mass and energy transfer, high reproducibility and simplification of manipulations.[125] Large-scale industrial ultrasonic devices have been successfully used in the food, cosmetic and pharmaceutical areas.[125] On the other hand, ILs have also been investigated for extraction processes for their solvation properties, high chemical stability and the tuning opportunities that they offer.[126] Recently, ultrasonic-assisted extraction in ILs has become an efficient approach, especially to reduce the reaction time and facilitate the procedures. For example, Cao *et al.* extracted piperine from white pepper *via* an ultrasonic pretreatment (bath, 40 kHz) in imidazolium based ILs.[127] The procedure only consisted of treating the sample powder in a water/IL mixture with low frequency ultrasound, and after filtration and dilution, the solution was analyzed by UPLC. No effects attributable to the ILs were observed on peak resolution, elution order and elution time. Liquid-phase micro-extraction for determination of aromatic amines in water samples also used the same kind of procedure showing the performance, simplicity, stability, low cost, ease of operation and low consumption of organic solvents offered by this method.[128]

Thus, a synergistic IL/US combination has been extensively demonstrated in the efficient extraction and microextraction of organic compounds from liquid or solid products, coupled to different analysis techniques such as chemiluminescence detection,[129] GC-MS,[130] HPLC,[131] high-speed counter-current chromatography,[132] flame atomic absorption spectrometry,[133] liquid chromatography-quadrupole-linear ion trap-mass spectrometry[134], fluorescence detection,[135] etc. The origins of the synergy is certainly related to mass transport effects at the micro- and nano-levels, the US compensating for the elevated viscosity of the ILs.

4.4. Lignocellulosic biomass valorization

Recently, the IL/US combination was investigated in the biomass conversion area.[136] Indeed, Rogers *et al.* have discussed IL based strategies for a better utilization of lignocellulosic biomass, highlighting the main advantages of these unconventional solvents including: (1) simple dissolution of cellulose, and possible regeneration for development of advanced materials, (2) direct dissolution of lignocellulosic biomass with separation of major components for direct use of the resulting biopolymers, (3) homogeneous dispersion for a facile depolymerization into low molecular weight chemicals, and (4) a facile pretreatment of wood for the access of enzymes or chemicals to react more easily.[137]

In 2007, Mikkola *et al.* functionalized microcrystalline cellulose, cotton linters and Kraft cellulose (carboxyethylation and carbopropylation) in the presence of 2-chloropropanoic acid or 2-chlorobutanoic acid using high-intensity ultrasound (frequency not clearly indicated, but probably low frequency).[138] The process involved ILs (1-allyl-3-methylimidazolium chloride or 1-butyl-3-methylimidazolium chloride) which are able to dissolve the biopolymer in a few minutes (5 to 22 min) under ultrasound. In this case, ultrasound enhanced the dissolution procedure, without any negative effects on the cellulose units. However, the functionalization part was not performed under ultrasound, but under classical stirring.

Rogers *et al.* also reported that an ultrasonic pretreatment (42 kHz ultrasonic bath, 135 W) improved the dissolution of cellulose in 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc])[139] and facilitated the separation of lignin and hemicellulose components in choline acetate ([Cho][OAc]).[140] Liu *et al*. used an ultrasonic probe (frequency not indicated, probably less than 50 kHz, 20–75 W) to dissolve cellulose in 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl). An increase of ultrasonic power (from 20 to 50 W) and irradiation time (from 0 to 20 min) resulted in the decrease in cellulose dissolution time (from 147 to 100 min, and from 190 to 60 min, respectively).[141] The FT-IR spectra measured for regenerated cellulose samples, after dissolution in [C_4mim]Cl with or without ultrasound irradiation, were similar except for the maximum ultrasonic power used (75 W) giving a peak from anti-symmetric stretching of carboxylic anions. This observation indicated that ultrasound with high power (beyond some arbitrary level) results in oxidative degradation of the cellulose. Ju *et al.* explained that ultrasonic treatment improved the solubility of cellulose because it facilitated the penetration and diffusion of 1-allyl-3-methylimidazolium into the structure of the samples.[142] Another study reported the combination of ball-milling and ultrasound pretreatment for dissolution of holocellulose in [C_4mim]Cl, reducing the dissolution time by seven fold.[143] After this dissolution treatment and the regeneration, holocellulose did not exhibit any chemical structure changes.

In this area, the most studied application of the IL/US combination is in the pretreatment of cellulose or lignocellulosic biomass to enhance enzymatic reactions.[144–151] For example, the cellulose saccharification ratio of bamboo powder pretreated in choline acetate was 1.7 times more efficient in the presence of low frequency ultrasound, and at room temperature (compared to 110 °C in silent conditions).[151] In the same way, ultrasonic pretreatment in imidazolium based ILs enhanced the enzymatic hydrolysis of kenaf powders.[149] ILs could access the cellulose and disrupt the hydroxyl bonds more efficiency during sonication through mass transfer improvement. Yu *et al.* showed that, in the sonochemical driven enzymatic isomerization of glucose to fructose in imidazolium ILs, the association of the two technologies helped to off-set the disadvantages of the cavitation effect on the enzyme caused by ultrasound as well as the mass transfer limitations caused by the high viscosity of the IL.[148]

Ma *et al.* optimized the glutarylation of surgarcane bagasse cellulose in 1-butyl-3-methylimidazolium chloride under ultrasound irradiation without a supplementary catalyst in the medium.[152] This method is relatively efficient for the one step preparation of cellulose glutarates using short reaction times and available sugarcane bagasse. Similarly, Hu *et al.* prepared reducing sugars from soybean or corn straw in different methylimidazolium based ILs and under ultrasound (low frequency, ultrasonic bath).[153] Very recently, Hernoux-Villière *et al.* converted starch-based industrial waste (potato peels) into reducing sugars in 1-allyl-3-methylimidazolium chloride and 1-(4-sulfobutyl)-3-imidazolium chloride.[154] Microwave and low frequency ultrasound activations were investigated to perform the depolymerization of the raw starch based material; only microwaves appeared to reduce the reaction time by reaching the required temperature in a short time period. The ultrasonic bath was not powerful enough to allow the mixing of a highly heterogeneous and viscous system that requires the use of an ultrasonic probe directly immersed in the solution for a direct irradiative mode.

Guo *et al.* used a Bronsted acidic IL as catalyst instead of as a solvent for the production of biodiesel from soybean.[155] Thus, in methanol and under ultrasonic conditions (24 kHz, 200 W), the methyl ester conversion reached 93.2% after 60 min. It appears that the IL/US combination should be, after optimization of all the parameters, an efficient and eco-friendly tool for synthesis of biodiesel.[156]

5. Degradative treatment of ionic liquids under ultrasound

With the growing use of ILs as solvents, they could soon be present in technological wastewasters, at trace levels.[157] As a result of their high chemical stability, they could then become persistent pollutants and break through classical treatment systems into natural waters. However, we do not know exactly the toxicity towards cells and environment, and the millions of possible cation/anion combinations lead to a complex evaluation of their impact on health and environment.[158] Hence degradative processes that could be applied as a waste treatment strategy are of importance to the field.

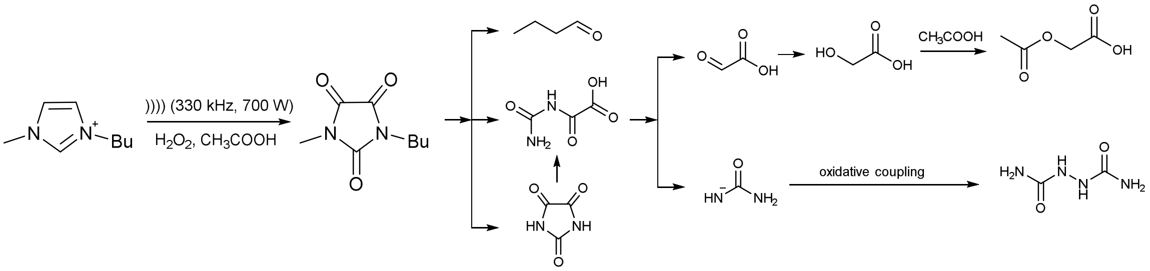


Figure 10: Oxidation degradation mechanism of C_4mim^+ cation under high frequency ultrasound.[159]

In 2007, Li *et al.* developed an efficient process for oxidative degradation of 1,3-dialkylimidazolium ILs in hydrogen peroxide and acetic acid medium under high frequency ultrasound (330 kHz, 750 W).[159] The authors achieved a degradation efficiency of 93% after 12 h, and 99% after 72 h. Degradation products were determined using GC-MS to propose a possible mechanism of degradation. In fact, three hydrogen atoms in the imidazolium ring were preferentially oxidized, followed by cleavage of the alkyl groups attached to the N atoms from the ring. Selective fragmentations of C–N bonds of the imidazolium ring lead to ring opening, forming degraded intermediates.

Recently, Wang *et al.* employed an ultrasonic and zero-valent iron activated carbon micro-electrolysis system to degrade 1-butyl-3-methylimidazolium chloride residues in water.[160] A low frequency ultrasonic bath (45 kHz, 300 W) was used. More than 81% of $[C_4mim]Cl$ was mineralized after a 110 min degradation reaction. The authors suggested that the imidazolium ring was oxidized to 1-butyl-3-methyl-2,4,5-trioxoimidazolidine, and then the ring was opened to form *N*-butylformamide and small molecular compounds. The authors demonstrated the efficiency of this method on different ILs showing that the degradation mechanism was dependent of the nature of the IL.[161] However, this technique has only been applied to treatment of low concentrations of IL in water (about 1 $mmol.L^{-1}$) and investigation of higher concentrations would be an important step. Thus it appears that the US irradiation provides a valuable approach to the destruction of ILs in, at least small-scale, waste streams and has the potential to be scaled up to a continuous larger-scale process by appropriate engineering design.

6. Recommendations and conclusions

Our literature review clearly shows that, in the last fifteen years, the use of ultrasound is increasingly investigated in the presence of, or for the synthesis of, ILs. The main areas where this synergistic combination are applied are organic chemistry, the synthesis of ILs, and more recently for materials preparation (catalysts, nanoparticles, nanotubes, propellants, etc), for extraction and micro-extraction, and for others applications (electrochemistry, sonochemical degradation of ILs, etc). As we have described in this review, the use of low frequencies is predominant with IL media, probably for its ease of processing and its accessibility (ultrasonic baths or in some cases, ultrasonic probes). In this context the IL improves the physical effects of sonochemistry such as the generation of shockwaves, microjets, micro-convection, micro-emulsions, erosion, etc. Most often, the beneficial consequences are the decrease of reaction/preparation times with improvements in yield, selectivity and/or quality of the products, compared to silent conditions. In some cases unexpected results can also be obtained under ultrasonic irradiations, thereby offering the potential for new synthesis pathways. Increasingly, low frequency ultrasound in an IL medium is also particularly valuable in the extraction area, offering significant benefits in terms of processing time and energy reduction, efficiency in mass and energy transfer, high reproducibility and simplification of manipulations.

The increasing numbers of reported examples demonstrates the potential for further promising opportunities to emerge from the IL/US combination. We especially identify the following important issues, trends and potentials:

(1) There is huge scope for more detailed investigation of the mechanisms involved in US irradiation in ILs. This is true for all uses of ultrasound, but even more so when ILs are chosen as propagation media since the low volatility of the IL represents an extreme regime for the cavitation phenomena. Rigorous characterization of sonochemical parameters is *essential* in terms of reproducibility and to clearly understand the associated chemistry. The lack of specific data about experimental conditions in numerous publications is striking and is certainly hold back progress in the field. Often, ultrasonic parameters are not detailed enough: the frequency, an essential parameter in term of ultrasonic effects, is not always indicated, the provided powers are often not completely clear (electric power, acoustic power, method of determination not provided), nor is the means of irradiation always specified (indirect irradiation in ultrasonic bath or direct irradiation *via* a probe). The importance of reactor geometries should be also taken into account and described, and some comparison between different shapes could be made. Finally, a systematic comparison with corresponding silent conditions is required to clearly highlight the ultrasonic effects. Concerning ILs, the purity, identity of likely impurities and the water content of the ILs is a very significant issue in this context and should be clearly specified in all experimental sections. Indeed, these issues remain a challenge broadly in the synthesis and use of ILs.

(2) The most important challenge of the IL/US combination is to find the right balance in terms of acoustic power delivered to the reaction medium. At low frequencies, it is necessary to provide enough energy to favor the physical effects. In many cases, the highly heterogeneous and viscous systems obtained in ILs require a direct irradiative mode *via* an ultrasonic probe directly immersed in the solution, since ultrasonic baths are not always sufficiently powerful. However, depending on the IL nature and purity, an acoustic power that is too high can cause partial (even at trace level) degradation of the IL. Many papers report the darkening of the irradiated IL as a function of the time; this represents a real issue for industrial applications and might be sufficient to deem the process impractical. It is not adequate for authors to presume that such issues will be solvable by further optimization and downstream processing. In addition, the means to recover/recycle the IL at the end of process remains challenging since such processes are may be significant consumers of organic solvents and energy.

(3) The presence of water or organic impurities in irradiated ILs impact significantly on the acoustic cavitation phenomenon. For example, in a water/hydrophobic IL medium submitted to 20 kHz US irradiation, the hot spots occur preferentially in water rather than in the IL.[61] The main explanations are the difference of viscosities and vapor pressures between water and IL. Indeed, the acoustic cavitation could depend on the viscosity of the irradiated

medium.[162] The addition of water to an IL (or a water containing IL) can "protect" it from degradation by pyrolysis, while maintaining the desired mechanical effects.[61] This direction needs to be investigated in depth and could represent an opportunity to avoid the darkening and degradation of ILs under ultrasonic irradiation in many reported examples. Intentional spiking with water at low levels is recommended as a vital supplementary experiment in all reports that involve "pure" ILs, in order to demonstrate the positive and/or negative effects of the presence of water. The choice of the IL nature and purity could also be an essential parameter to impact the cavitation and limit the degradation.

(4) In the presence of ILs, typically only the physical effects of ultrasound have been researched since the production of radicals at high frequency (or at low frequency, in the presence of an iron catalyst for example, via a Fenton reaction)[163] causes important and rapid degradation of ILs. High frequency ultrasound seems currently to be mostly of interest only as a means for IL degradation *via* advanced oxidation processes.[159] The transition between these regimes and its dependence on the chemical nature of the IL ions needs to be further explored in order to provide a basis for optimising IL based media.

(5) We can also note that the IL/US combination opens the door to interesting opportunities in new research areas. For example, we have seen that the combined technology produces exciting results for biomass pretreatment.[144–151] The combination with other innovative technologies represents a great potential in term of innovation, for example coupling with enzymatic catalysis for enhancing enzymatic activity in ILs.[51] In these cases, it will be important to study silent, coupled and non-coupled conditions separately, for comparison and to highlight the synergetic effects.

Based on the numerous advantages discussed here, in terms of time reduction, yield improvement, energy economy and innovation, this US/IL combination clearly has a strong potential to contribute to innovation broadly in green and sustainable chemistry. The challenge will also be, through systematic energy consumption studies, to demonstrate the energetic and financial competitiveness of these methods in comparison to existing processes performed in silent conditions.

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