Journal of Molecular Liquids 211 (2015) 934–937

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Sonochemical synthesis and characterization of imidazolium based ionic liquids: A green pathway

Garima Ameta [a], Arpit Kumar Pathak [a], Chetna Ameta [a], Rakshit Ameta [b], Pinki B. Punjabi [a,*]

[a] Photochemistry Laboratory, University College of Science, Mohanlal Sukhadia University, Udaipur, 313002 Raj., India
[b] Deparment of Chemistry, PAHER University, Udaipur, 313003 Raj., India

ARTICLE INFO

Article history:
Received 23 May 2015
Received in revised form 31 July 2015
Accepted 4 August 2015
Available online xxxx

Keywords:
Green synthesis
Ultrasonic irradiation
Imidazolium-based ionic liquids
Spectroscopy

ABSTRACT

The emerging importance of sonochemistry as "green" process and ionic liquids (ILs) as "green" materials with their wide applications are rapidly increasing. Imidazolium-based ionic liquid derivatives are synthesized using a facile and green ultrasound-assisted procedure. Their structures were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and Mass spectroscopy. The main advantages of the present procedure as compared with conventional method are mainly, its milder conditions, shorter reaction time, higher yields and selectivity without the need for a transition metal or base catalyst.

1. Introduction

Ionic liquids have been studied extensively as green solvents because of their tempting properties such as negligible vapor pressure, large liquidus range, high thermal stability, higher ionic conductivity, large electrochemical window and ability to solvate compounds of widely varying polarity [1–3]. Utilization of ionic liquids as solvent is one of the goals of green chemistry because these provide a cleaner and more sustainable chemistry and are receiving increasing interest as environmental friendly solvents for many synthetic and catalytic processes [4–8]. An intriguing characteristic is that their the physicochemical properties of ILs may be finely tuned as per the requirement by suitable choice of cations and anions. Therefore, ionic liquids have been recognized as "designer-solvents" [9]. The unique properties of ionic liquids, such as very low volatility, nonflammability and stability make them suitable for use in a variety of different areas, such as organic synthesis, (bio)catalysis, electrochemistry, analytical chemistry, separation technology, nanotechnology, renewable resource utilization and its use as functional fluids (e.g., lubricants, heat transfer fluids, corrosion inhibitors) [10].

It is worth mentioning that, application of ultrasound has received significant attention in the chemical and pharma industries during the last two decades. Its goal is to meet the needs of green chemistry as a promising pathway to the design, manufacture and use of chemical products in order to reduce or eliminate chemical hazards by choosing the safest and the most efficient way for their synthesis [11,12]. The influence of ultrasound on a chemical reaction is attributed to the formation of cavitations, which are induced by the ultrasonic waves and their collapse can release very high local temperature and pressure. Enhancement in reaction rates and yield of product in both heterogeneous and homogenous systems have been well documented [13,14]. Conventionally, the synthesis of ionic liquids via quaternization of tertiary amine species has been performed in stirred tanks using batch or semi batch processes. Although looks quite simple, but these processes are excessively time- and energy-consuming [15]; therefore, sustainable nonconventional techniques for process intensification have been the subject of considerable recent attention. Synthesis of ionic liquids through ultrasonic waves is an emerging green technology [16], as it claims a drastic decrease in the reaction time. An efficient single-stage synthesis of several imidazolium-based ionic liquids with fluorinated anions using low-frequency ultrasound has been described [17]. Since then, a number of reports on successful ultrasound-assisted ionic liquids' syntheses have confirmed the benefit of their application at the laboratory scale [18].

Herein, we report the sonochemical synthesis and characterization of some new 1,3-dibutylimidazolium based ionic liquids.

2. Materials and methods

All chemicals used in this study were of analytical reagent grade and used as received. Imidazole (Himedia, India), n-BuLi (Sigma-Aldrich, India), n-butyl bromide (CDH, India), and dichloromethane (Fisher Scientific, India) were used as received. Sodium tetrafluoroborate, silver sulphate, sodium trifluoromethane sulphonate and p-toluene sulphonic acid (Himedia) were also used as supplied. Ultrasonic cleaner 392

---

* Corresponding author.
E-mail address: pb_punjabi@yahoo.com (P.B. Punjabi).

http://dx.doi.org/10.1016/j.molliq.2015.08.009
0167-7322/© 2015 Published by Elsevier B.V.

(Systronics) was used for ultrasonic irradiation with a frequency of 40 kHz and a nominal power of 115 W.

3. Experimental

All reactions were carried out in an ultrasonic bath. The synthesis of ionic liquids involves three steps (Scheme 1).

Step I — 1-butylimidazole was synthesized by N-alkylation of imidazole (0.1 mol) with n-butyl lithium (0.1 mol) in ethanol under the influence of ultrasound for 3 h at room temperature. The progress of the reaction was monitored by TLC.
Step II — Reaction of 1-butylimidazole (0.1 mol) with 1-bromobutane (0.1 mol) was carried out in the presence of ultrasonic waves for 2.5 h at 10 ° C to form 1,3-dibutylimidazolium bromide (ionic liquid) by quaternization method. The bromide salt was dissolved in dichloromethane and then extracted with ether. The muddy solution was kept at room temperature to become transparent as some precipitates settle down. Then, the solution was filtered and the purification was carried out three times. Finally, the salt was obtained after pumping out the trace solvent in vacuum.
Step III — Anion metathesis is the methodology of choice for the preparation of water and air stable ionic liquids based upon 1,3-dialkylimidazolium cations. This method involves the treatment of the halide salt with the silver/sodium/potassium salts of BF_4^-, SO_4^{2-}, TfO$^-$ and Tos$^-$ or free acid of the appropriate anion.

In the presence of ultrasound, reaction of 1,3-dibutylimidazolium bromide ([BBIM] Br) was carried out either with sodium tetrafluoroborate, silver sulphate, sodium trifluoromethyl sulphonate (sodium triflate) or p-toluene sulphonic acid to give 1,3-dibutylimidazolium tetrafluoroborate (Step III case I), 1,3-dibutylimidazolium sulphate (Step III case II), 1,3-dibutyl imidazolium trifluoromethyl sulphonate (triflate) (Step III case III) and 1,3-dibutylimidazolium p-toluene sulphonate (tosylate) (Step III case IV) ionic liquids, respectively in dry acetone. These ionic liquids were dissolved in dichloromethane, which were further extracted with ether for purification. The muddy solution was kept at room temperature to become transparent. The solutions were then filtered and the purification was carried out three times. Finally, the salts were obtained after pumping out the trace solvent in vaccum.

Preparation of dry acetone — Dry $MgSO_4$ was kept in an oven for 1 h to evaporate H_2O. 3 g of $MgSO_4$ was mixed with 50 mL of acetone with continuous stirring (5 h). Thereafter, it was allowed to stand overnight to get dry acetone.

4. Results and discussion

A Perkin-Elmer spectrum-2000 Fourier transform IR spectrophotometer (USA) was used to obtain the IR spectra between 400 and 4000 cm^{-1}. The samples were prepared in pellet form using spectroscopic grade KBr. ^{1}H-NMR and ^{13}C-NMR spectra were recorded by multinuclear FTNMR spectrometer Model Avance-II (Bruker). The instrument was equipped with a cryomagnet of field strength 9.4 T. Its ^{1}H frequency was 400 MHz, while for ^{13}C the frequency was 100 MHz. Waters, Q-Tof micro Mass spectrometer (LC–MS) was used for mass spectral analysis of synthesized ionic liquids.

4.1. FTIR spectra

4.1.1. 1,3-Dibutylimidazolium bromide ([BBIM] Br)

IR (KBr, cm^{-1}): C–H stretching — 2874 cm^{-1}, CH_2 bending — 1464 cm^{-1}, CH_3 bending — 1378 cm^{-1}, =CH stretching — 3137 cm^{-1}, N–C stretching — 1260 cm^{-1} and 3080 cm^{-1}, C=C stretching — 1645 cm^{-1} and C=N stretching — 1632 cm^{-1}.

4.1.2. 1,3-Dibutylimidazolium tetrafluoroborate ([BBIM] BF_4)

C–H stretching — 2850 cm^{-1}, CH_2 bending — 1446 cm^{-1}, CH_3 bending — 1368 cm^{-1}, =CH stretching — 3061 cm^{-1}, N–C stretching — 1287 cm^{-1} and 3095 cm^{-1}, C=C stretching — 1653 cm^{-1}, C=N stretching — 1664 cm^{-1} and B–F stretching — 1453 cm^{-1}, 712 cm^{-1} and 481 cm^{-1}.

4.1.3. 1,3-Dibutylimidazolium sulphate ([BBIM] SO_4)

C–H stretching — 2868 cm^{-1}, CH_2 bending — 1462 cm^{-1}, CH_3 bending — 1380 cm^{-1}, =CH stretching — 3133 cm^{-1}, N–C stretching — 1272 cm^{-1} and 3051 cm^{-1}, C=C stretching — 1646 cm^{-1}, C=N stretching — 1639 cm^{-1}, S=O stretching — 1167 cm^{-1} and S–O stretching — 949 cm^{-1}.

4.1.4. 1,3-Dibutylimidazolium p-toluene sulphonate ([BBIM] Tos)

C–H stretching — 2875 cm^{-1}, CH_2 bending — 1461 cm^{-1}, CH_3 bending — 1383 cm^{-1}, =CH stretching — 3109 cm^{-1}, N–C stretching — 1333 cm^{-1} and 2963 cm^{-1}, C=C stretching — 1601 cm^{-1}, C=N stretching — 1719 cm^{-1}, C=C stretching (conjugation) — 1629 cm^{-1}, C–H in plan — 1399 cm^{-1}, C–H bend (para) — 817 cm^{-1}, S=O stretching — 1383 cm^{-1} and S–O stretching — 753 cm^{-1}.

4.1.5. 1,3-Dibutylimidazolium tetrafluoromethane sulphonate ([BBIM] TfO)

C–H stretching — 2939 cm^{-1}, CH_2 bending — 1466 cm^{-1}, CH_3 bending — 1371 cm^{-1}, =CH stretching — 3112 cm^{-1}, N–C stretching — 1256 cm^{-1} and 2966 cm^{-1}, C=C stretching — 1639 cm^{-1}, C=N stretching — 1632 cm^{-1}, S=O — 1371 cm^{-1}, S–O — 851 cm^{-1} and C–F stretching (trifloromethyl— 2 strong broad bands) — 1166 cm^{-1} and 1256 cm^{-1}.

4.2. NMR spectra

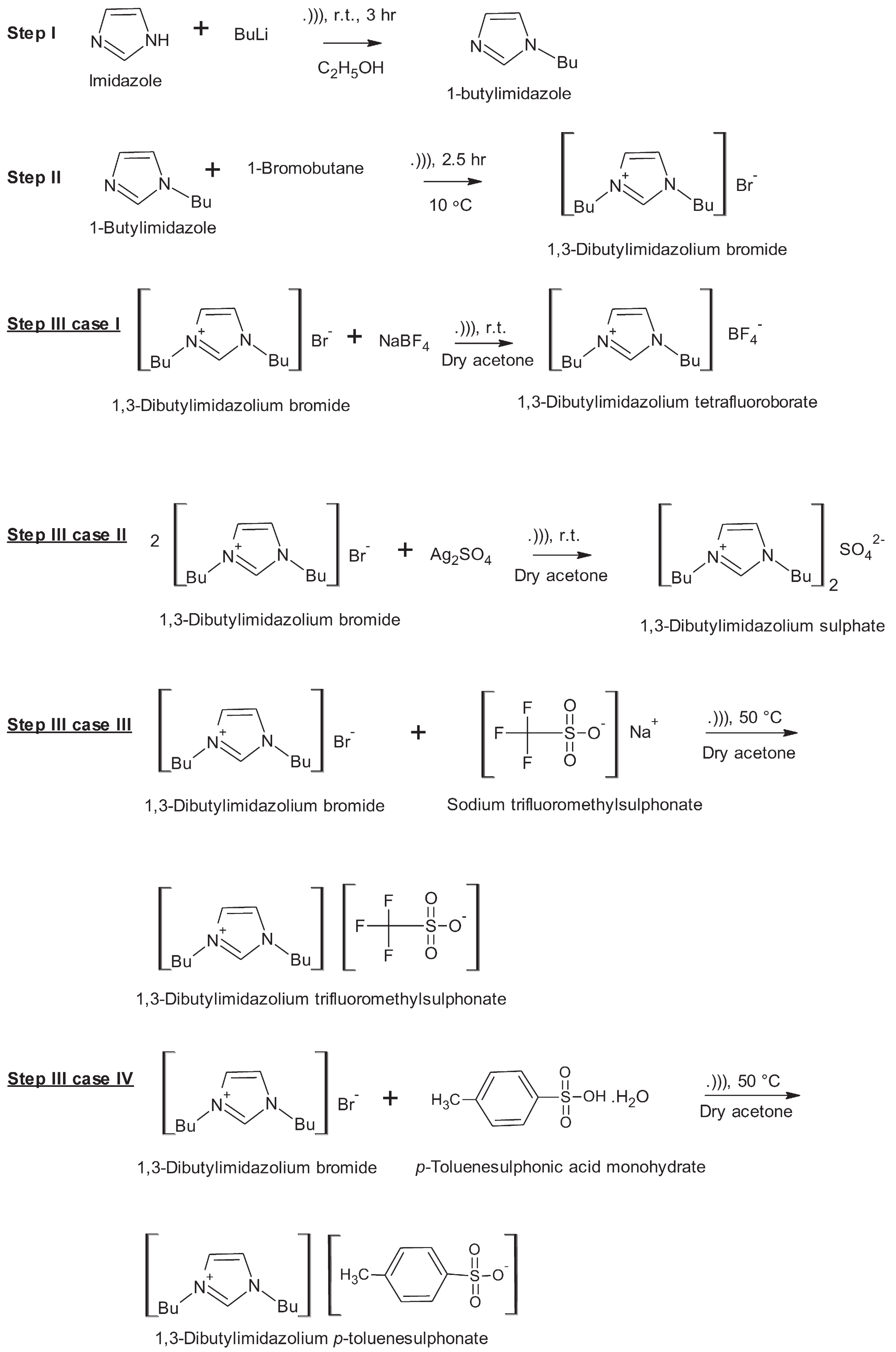
1,3-Dibutylimidazolium bromide ([BBIM] Br) — ^{1}H-NMR ($CDCl_3$, 400 MHz): δ ppm = 0.90 (t, ^{9}CH), 1.29 (m, ^{8}CH), 2.01 (m, ^{7}CH), 4.94 (t, ^{6}CH), 7.51 (t, ^{5}CH), 7.86 (t, ^{4}CH), 8.86 (s, ^{2}CH); ^{13}C-NMR ($CDCl_3$, 100 MHz): (δ ppm): 12.98 (^{9}CH), 20.49 (^{8}CH), 32.23 (^{7}CH), 51.46 (^{6}CH), 122.84 (^{4}CH), 124.65 (^{5}CH) and 138.23 (^{2}CH).

1,3-Dibutylimidazolium tetrafluoroborate ([BBIM] BF_4) — ^{1}H-NMR ($CDCl_3$, 400 MHz): δ ppm = 0.83 (t, ^{9}CH), 1.32 (m, ^{8}CH), 1.91 (m, ^{7}CH), 4.29 (t, ^{6}CH), 7.74 (t, ^{5}CH), 7.81 (t, ^{4}CH), 8.69 (s, ^{2}CH); ^{13}C-NMR ($CDCl_3$, 100 MHz): (δ ppm): 13.11 (^{9}CH), 19.99 (^{8}CH), 31.32 (^{7}CH), 55.39 (^{6}CH), 121.53 (^{4}CH), 124.60 (^{5}CH) and 139.03 (^{2}CH).

1,3-Dibutylimidazolium sulphate ([BBIM] SO_4) — ^{1}H-NMR ($CDCl_3$, 400 MHz): δ ppm = 0.85 (t, ^{9}CH), 1.23 (m, ^{8}CH), 1.99 (m, ^{7}CH), 5.12 (t, ^{6}CH), 7.68 (t, ^{5}CH), 7.97 (t, ^{4}CH), 8.65 (s, ^{2}CH); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ ppm = 13.84 (^{9}CH), 23.56 (^{8}CH), 24.48 (^{7}CH), 13.82 (^{6}CH), 122.12 (^{4}CH), 116.48 (^{5}CH) and 138.94 (^{2}CH).

1,3-Dibutylimidazolium p-toluenesulphonate ([BBIM] Tos) — ^{1}H-NMR ($CDCl_3$, 400 MHz): δ ppm = 0.86 (t, ^{9}CH), 1.24 (m, ^{8}CH), 2.24 (m, ^{7}CH), 5.21 (t, ^{6}CH), 7.68 (t, ^{5}CH), 8.12 (t, ^{4}CH), 9.03 (s, ^{2}CH), 2.35 (^{e}CH), 7.38 (^{c}CH), 7.68 (^{b}CH); ^{13}C-NMR ($CDCl_3$, 100 MHz): (δ ppm): 13.28 (^{9}CH), 19.15 (^{8}CH), 31.71 (^{7}CH), 49.52 (^{6}CH), 121.71 (^{4}CH), 122.51 (^{5}CH), 135.33 (^{2}CH), 21.23 (^{e}CH), 140.09 (^{d}CH), 129.07 (^{c}CH), 125.73 (^{b}CH) and 141.03 (^{a}CH).

1,3-Dibutylimidazolium tetrafluoromethanesulphonate ([BBIM] TfO) — ^{1}H-NMR ($CDCl_3$, 400 MHz): δ ppm = 0.91 (t, ^{9}CH), 1.31 (m, ^{8}CH), 1.89 (m, ^{7}CH), 4.24 (t, ^{6}CH), 7.65 (t, ^{5}CH), 7.71 (t, ^{4}CH), 8.96 (s, ^{2}CH); ^{13}C-NMR ($CDCl_3$, 100 MHz): (δ ppm): 13.04 (^{9}CH), 19.20 (^{8}CH), 32.35 (^{7}CH), 49.46 (^{6}CH), 121.63 (^{4}CH), 122.39 (^{5}CH), 136.97 (^{2}CH) and 135.22 (^{a}CH).



Scheme 1. Ultrasound-assisted synthesis of 1,3-dibutylimidazolium based ionic liquids.

4.3. Mass spectra

1,3-Dibutylimidazolium bromide ([BBIM] Br) — 181.2 ($C_{11}H_{21}N_2$), 124.1 ($C_7H_{12}N_2$)

1,3-Dibutylimidazolium tetrafluoroborate ([BBIM] BF_4) — 181.2 ($C_{11}H_{21}N_2$), 124.1 ($C_7H_{12}N_2$), 67.8 (BF_3)

1,3-Dibutylimidazolium sulphate ([BBIM] SO_4) — 181.2 ($C_{11}H_{21}N_2$), 124.1 ($C_7H_{12}N_2$)

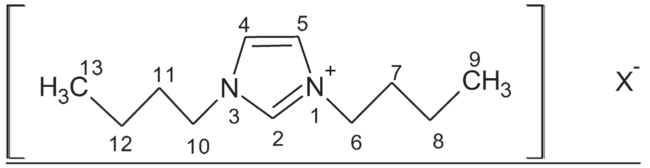


Fig. 1. The chemical structure of 1, 3-dibutylimidazolium ionic liquid, where X = Br^-, BF_4^-, SO_4^{2-}, TfO and Tos.

1,3-Dibutylimidazolium p-toluenesulphonate ([BBIM] Tos) — 181.2 ($C_{11}H_{21}N_2$), 124.1 ($C_7H_{12}N_2$), 171.2 ($C_7H_7O_3S$), 156.1 ($C_6H_4O_3S$), 15 (CH_3), 91 (C_7H_7)

1,3-Dibutylimidazolium tetrafluoromethanesulphonate ([BBIM] TfO) — 181.2 ($C_{11}H_{21}N_2$), 124.1 ($C_7H_{12}N_2$), 149 (CF_3O_3S)

4.4. Viscosity

Ionic liquids are viscous liquids as compared to the conventional organic solution, being 1–3 orders of magnitude higher. This high viscosity will adversely affect the operating process. The viscosities of ionic liquids are governed essentially by Van der Waals interactions and H-bonding. Alkyl chain lengthening or fluorination makes the salt more viscous, due to an increase in Van der Waals interactions and hydrogen bonds (Fig. 1). Alkyl chain ramification also increases the viscosity due to reduced rotation freedom. Viscosities of the ionic liquids were measured by DV-I (II) Viscometer (Brookfield). Viscosities of different synthesized ionic liquids are given in Table 1.

4.5. Conductivity

Ionic liquids are composed of only ions; therefore, they show very high ionic conductivity, thermal stability and nonflammability. Nonflammable liquids with high ionic conductivity are practical materials for use in electrochemistry. The conductivities of different ionic liquids were measured by conductivity cell (Systronics Model 305). Conductivities of different synthesized ionic liquids are reported in Table 1.

5. Conclusion

It is clear from the observations that large number of ionic liquids can be synthesized by simple combination of different cations and anions. The ionic liquids find applications as storage media for toxic gases, catalysts/solvents in organic syntheses, electrolytes, performance additives in pigments, and matrices because of their “tailor-made” nature. Ultrasound assisted synthesis of ionic liquids has an edge over classical conventional methods, i.e., ecofriendly nature, simple product isolation, higher yield and shorter reaction times. Therefore, introduction of such an efficient synthetic protocols should lower down the cost of ionic liquids; thus, encourages a wider use of these neoteric solvents.

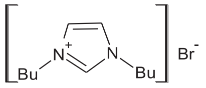
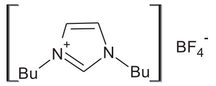
Acknowledgments

One of the authors (Dr. Garima Ameta) is thankful to University Grants Commission (F.15-1/2011-12/PDFWM-2011-12-GE-RAJ-9578(SA-II)), New Delhi for providing financial assistance in the form of Post Doctoral Fellowship. We are thankful to Prof. Suresh C. Ameta for giving valuable suggestions during the progress of the work. We are also thankful to the Director, SAIF and CIL, Chandigarh, India for providing spectral data.

References

[1] D.M. Eike, J.F. Brennecke, E.J. Maginn, Predicting melting points of quaternary ammonium ionic liquids, Green Chem. 5 (2003) 323–328.
[2] J.D. Holbrey, K.R. Seddon, The phase behaviour of 1-alkyl-3-methylimidazolium tetrafluoroborates: ionic liquids and ionic liquid crystals, J. Chem. Soc. Dalton Trans. 13 (1999) 2133–2139.
[3] P.A.Z. Suarez, S. Einloft, J.E.L. Dullius, R.F. Souza, J. Dupont, Synthesis and physical–chemical properties of ionic liquids based on 1-n-butyl-3-methyl imidazolium cations, J. Chim. Phys. Phys.-Chim. Biol. 95 (1998) 1626–1639.
[4] F. Endres, S.Z.E. Abedin, Air and water stable ionic liquids in physical chemistry, Phys. Chem. Chem. Phys. 8 (2006) 2101–2116.
[5] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, second ed. VCH-Wiley, Weinheim, 2007.
[6] M.J. Earle, K.R. Seddon, Ionic liquids. Green solvents for the future, Pure Appl. Chem. 72 (2000) 1391–1398.
[7] P. Wasserscheid, W. Keim, Ionic liquids—new “Solutions” for transition metal catalysis, Angew. Chem., Int. Ed., 39 2000, pp. 3772–3789.
[8] D.W. Rooney, K.R. Seddon, in: G. Wypych (Ed.), Handbook of Solvents, ChemTec, Toronto 2000, p. 1495.
[9] M. Freemantle, Designer solvents, ionic liquids may boost clean technology development, Chem. Eng. News 76 (1998) 32–37.
[10] D.D. Patel, J.M. Lee, Applications of ionic liquids, Chem. Rec. 12 (2012) 329–355.
[11] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998 30.
[12] R.A. Sheldon, Fundamentals of green chemistry: efficiency in reaction design, Chem. Soc. Rev. 41 (2012) 1437–1451.
[13] R.B. Nasir Baig, R.S. Varma, Alternative energy input: mechanochemical, microwave and ultrasound-assisted organic synthesis, Chem. Soc. Rev. 41 (2012) 1559–1584.
[14] S. Hübner, S. Kressirer, D. Kralisch, C. Bludszuweit-Philipp, K. Lukow, I. Jänich, A. Schilling, H. Hieronymus, C. Liebner, K. Jähnisch, Ultrasound and microstructures—a promising combination, ChemSusChem 5 (2012) 279–288.
[15] M. Deetlefs, K.R. Seddon, In Handbook of green chemistry, in: P. Wasserscheid, A. Stark (Eds.), Ionic Liquids, Volume 6, Wiley-VCH Verlag GmbH & Co, Weinheim 2010, pp. 1–38.
[16] V.V. Namboodiri, R.S. Varma, Solvent-free sonochemical preparation of ionic liquids, Org. Lett. 4 (2002) 3161–3163.
[17] J.M. Léveque, J.L. Luche, C. PetrIer, An improved preparation of ionic liquids by ultrasound, Green Chem. 4 (2002) 357–360.
[18] J.M. Léveque, J. Estager, M. Draye, G. Cravotto, L. Boffa, W. Bonrath, Synthesis of ionic liquids using non conventional activation methods: an overview, Monatsh. Chem. 138 (2007) 1103–1113.

Table 1
1, 3- Dibutylimidazolium-based ionic liquids.

S.N.	Structural formula	Reaction time in Ultrasound (Hours)	Yield (%)	Viscosity η/cp	Conductivity (S/m)
1	 1,3-Dibutylimidazolium bromide [BBIM] Br	2.5	95	613	0.23
2	 1,3-Dibutylimidazolium tetrafluoro borate [BBIM] BF_4	3.0	79	373	0.17