

Synthesis and characterization of neoteric green solvent 1-benzylimidazolium cation based brønsted acidic ionic liquids

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Abstract: Synthesis of 1-benzylimidazolium cation based brønsted acidic ionic liquids from the reaction of 1-benzylimidazole and protic acid with counter anions such as BF_4^- , PF_6^- , OTf^- , NO_3^- , CH_3SO_3^- , and $\text{C}_6\text{H}_5\text{SO}_3^-$ have reported. The ionic liquids were synthesized by direct neutralization and metathesis methods. The reactions are carried out in the presence of toluene. The structure of the reported ionic liquids has confirmed by ^1H NMR and mass spectrometry and their physical nature and melting point also discussed in this present paper.

Keywords: Brønsted acidic ionic liquid, reusable, recyclable, recovery of metals, thermal stability, neoteric solvent, green solvent and catalyst.

Introduction

RTILs have received greater attention towards the chemistry community over the past few years.¹ It acts as green solvent for many organic chemical transformation reactions such as Mannich, Bignelli, Beckmann, Ester hydrolysis *etc.* and also useful for the recovery of precious metals, separation of catalysts, electrochemical polymerization reactions. They belong to highly complex solvent system since the RTILs properties can be changed from acid to base.²⁻³ They cover the area of green chemistry with special results for the past one decade. All the ionic liquids are neoteric solvent and catalyst especially alkyl imidazolium salts acts as a good and clean green solvent.

Ionic liquids are low melting point organic salts, which are having notable properties such as low flammability, low volatility and wide liquid temperature range.⁴ Further more attractive properties such as polarity, viscosity and melting temperature can be changed with respect to counter anions. They have negligible vapor pressure, thermal stability, large electrochemical window, insoluble in super critical CO_2 and easily soluble in large range of organic molecules and transition metal complexes.⁵ They are applicable to recycle and reuse for chemical process in bio and chemical catalysis.⁶ Ionic liquids recognized as an environmentally benign alternative to common organic solvents.

There are two methods to synthesize ionic liquids a) Direct neutralization b) metathesis

a) Imidazolium based brønsted acid ionic liquid can be easily prepared by direct neutralization method. This is the simplest method to synthesize ionic liquid due to the basic nature of imidazole and acid nature of strong protic acids.⁷ They can easily form salts. b) 1-Alkyl imidazole treated with tertiary butyl bromide to form ionic liquid.⁸ On heating the released HBr gas from tertiary butyl bromide is abstracted by 1-alkylimidazole followed by conversion into desired ionic liquid. Different 1-alkyl imidazolium based brønsted ionic liquid can be prepared by using different alkali metal salts like NaBF_4 , KPF_6 , AgNO_3 and AgBr *etc.*⁹

Experimental Section

Toluene, hexane, dichloromethane and methanol were freshly distilled prior to use. Glassware was dried in oven at 120 °C overnight. Chemicals such as benzyl bromide, tert-butyl bromide, imidazole, acetic acid, glyoxal, paraformaldehyde, Ammonium carbonate were purchased from SD fine chemicals, India and used as received. Ammonium tetrafluoroborate, potassium hexafluorophosphate, silver nitrate were purchased from Aldrich chemicals and used as received. 1-benzyl imidazole was prepared by using chemical procedures.¹⁰ ¹H NMR spectra were recorded in 400 mhz. Mass spectrometry was performed on a Q-ToF premier [waters corporation] mass spectrometer operating in positive ion electro spray mode and methanol was used as a mobile phase. The capillary and cone voltages were set at 2.5kv and 39.0kv. The desolvation temperature was set to 350 °C and the source temperature was set to 100 °C. The cone gas was set to a flow rate of 30.0 L\Hr and the desolvation gas flow was maintained at 626.0 L\HR.

Synthesis of 1-benzylimidazolium based brønsted acidic ionic liquids.

Direct neutralization method

In a two neck flask, trifluoromethanesulfonic acid or methanesulphonic acid or benzenesulfonic acid (10 mmol) was added to a toluene (10 mL) solution of 1-benzylimidazole (10 mmol). The resulting mixture was heated to 80 °C and stirred for 16 h. The immiscible layers were separated by decanting the toluene and the sticky product was washed with hexane and dried over vacuum.

- 1-benzylimidazolium triflate (ImBzHTA): Pale yellow color liquid, yield 89 %, ¹H NMR (DMSO-d₆, 400 MHz): 9.03 (s, 1H, 2-CH), 7.77 (d, 1H, 4CH), 7.66 (d, 1H, 5CH), 7.39 (5H, Ar-H), 5.40 (s, 2H, benzylic-CH₂). ES-MS *m/z*: 159.0 [M-CF₃SO₃]⁺.
- 1-benzylimidazolium methanesulphonate (ImBzHMS): Pale yellow color liquid, yield 81 %, ¹H NMR (DMSO-d₆, 400 MHz): 9.21 (s, 1H, 2-CH), 7.77 (d, 1H, 4CH), 7.66 (d, 1H, 5CH), 7.36 (5H, Ar-H), 5.44 (s, 2H, benzylic-CH₂), 2.35 (s, 3H, CH₃SO₃). ES-MS *m/z*: 159.0 [M-CH₃SO₃]⁺.
- 1-benzylimidazolium benzenesulfonate (ImBzHPS): Off white solid, yield 86 %, m.p. 145 °C, ¹H NMR (DMSO-d₆, 400 MHz): 9.16 (s, 1H, 2-CH), 7.64 (d, 1H, 4CH), 7.61 (d, 1H, 5CH), 7.59 (m, 2H, C₆H₅SO₃), 7.39 (m, 5H, Ar-H), 7.30 (1H, C₆H₅SO₃), 7.12 (m, 2H, C₆H₅SO₃), 5.42 (d, 2H, benzylic-CH₂). ES-MS *m/z*: 159.2 [M-C₆H₅SO₃]⁺.

Metathesis method

Synthesis of 1-benzylimidazolium bromide.

In a two neck flask, tertiary butyl bromide was added to a toluene solution of 1-benzyl imidazole. The resulting mixture was heated to 80 °C and stirred for 16 h. The immiscible layers were separated by decanting the toluene and the sticky product was washed with hexane and dried over vacuum.

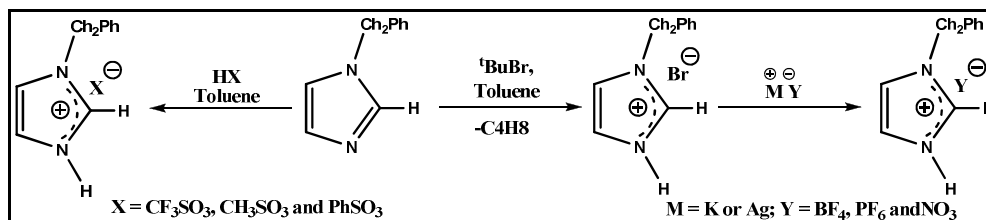
Metathesis followed by anion exchange method

15 mmol of ammonium tetrafluoroborate or potassium hexafluorophosphate or silver nitrate was added to a solution of 15 mmol of 1-isopropylimidazolium bromide in (50 mL) CH₂Cl₂ / CH₃OH (5:1). The resulting mixture stirred for 3 hours at room temperature. The solution was filtered and the solvents were removed by vacuum.

- 1-benzylimidazolium tetrafluoroborate (ImBzHTFB): Off white solid, yield 83 %. M.p. 95 °C. ¹H NMR (CDCl₃, 400 MHz): 9.24 (s, 1H, 2-CH), 7.78 (d, 1H, 4CH), 7.68 (d, 1H, 5CH), 7.38 (m, 5H, Ar-H), 5.43 (s, 2H, benzylic-CH₂). ES-MS *m/z*: 159.0 [M-BF₄]⁺
- 1-benzylimidazolium hexafluorophosphate (ImBzHHFP) : Off white semisolid, yield 78 %. ¹H NMR (CDCl₃, 400 MHz): 9.30 (s, 1H, 2-CH), 7.80 (d, 1H, 4CH), 7.70 (d, 1H, 5CH), 7.38 (m, 5H, Ar-H), 5.45 (s, 2H, benzylic-CH₂). ES-MS *m/z*: 159.0 [M-PF₆]⁺
- 1-benzylimidazolium nitrate (ImBzHN): Off white solid, yield 79 %. M.p. 75 °C. ¹H NMR (CDCl₃, 400 MHz): 9.22 (s, 1H, 2-CH), 7.78 (d, 1H, 4CH), 7.68 (d, 1H, 5CH), 7.38 (m, 5H, Ar-H), 5.43 (s, 2H, benzylic-CH₂). ES-MS *m/z*: 159.0 [M-NO₃]⁺

Results and discussion

We have performed experiments on toluene solution of 1-benzylimidazole with corresponding protic acids by heating the reaction mixture to 75°C till the clear visible two layer formation takes place. The brønsted acidic ionic liquids are soluble in polar protic solvent such as dimethyl sulfoxide, water, ethanol, methanol, dichloromethane, chloroform, dimethyl formamide and immiscible with non-polar solvents like hydrocarbon solvents.¹¹



Scheme 1: Synthesis of 1-benzylimidazolium cation based brønsted ionic liquids

The investigated 1-benzylimidazolium bromide, 1-benzyl imidazolium tetrafluoroborate, 1-benzyl imidazolium nitrate, 1-benzylimidazolium phenylsulfonate are solids, 1-benzylimidazolium triflate, 1-benzyl methane sulfonic acids are liquids, they have little vapor pressure. All the ionic liquids were characterized by H¹NMR and mass spectrometry. In the H¹NMR the 2-CH proton falls in the range of 9.03-9.24 ppm, the 4-CH proton ranges from 7.64-7.80 ppm. The value of Ar-H lies between 7.36-7.39 and benzylic CH₂ lies from 5.40-5.44. The chemical shift value of PF₆⁻ is high compared to other anions of the imidazole. The value of BF₄⁻ is just below of the PF₆⁻ then for 4-CH proton the value of PF₆⁻ is 7.80 for C₆H₅SO₃⁻ the value is 7.64. Moreover the positive ion gave the corresponding cationic ([M-X]⁺) peak falls in the range of 159.0 for all the all 1-benzylimidazolium cations and 1-benzyl imidazolium phenylsulfonate with the value of ([M-X]⁺) of 159.2. The increasing order of acidity of ionic liquids was based on chemical shift of 2-CH H¹NMR.

1-benzylimidazoliumhexafluorophosphate > 1-benzylimidazoliumtetrafluoroborate > 1-benzylimidazolium nitrate > 1-benzylimidazolium methane sulfonate > 1-benzylimidazolium phenyl sulfonate > 1-benzylimidazolium triflate.

Table 1: Spectral values of 1-isopropyl imidazolium based brønsted acidic ionic liquids

Ionic liquids	¹ H-NMR Value (ppm)			ESI-MASS (M/Z)
	2-CH	4-CH	5-CH	
ImBzHTA	9.03	7.77	7.66	159.0.
ImBzHMS	9.21	7.77	7.66	159.0.
ImBzHPS	9.16	7.64	7.61	159.2.
ImBzHTFB	9.24	7.78	7.68	159.0.
ImBzHHFP	9.30	7.80	7.70	159.0.
ImBzHN	9.22	7.78	7.68	159.0.

Conclusion

In conclusion we have synthesised and characterised six different examples of 1-benzylimidazolium based ionic liquids with different counter anionic substituents by simple neutralisation and metathesis method. Their H¹NMR and mass and physical nature also discussed. The comparison of different protons also reported in this paper.

Acknowledgement

The author thanks the Department of Science and technology, Science and Engineering Research board (DST-SREB,SR/FT/CS-60/2011) India for funding the project.

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