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Synthesis and structural characterization of 1-propyl benzimidazolium based acidic ionic liquids with some counter anions

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Abstract: In this paper we have discussed few examples of 1-propyl benzimidazolium cation based ionic liquids with different counter anions such as tetrafluroborate, hexaflurophosphate, nitrate, triflate, methane sulfonate, phenyl sulfonate. The reported ionic liquids have been confirmed by H^1-NMR, mass spectroscopy.

Introduction

Most of the organic solvents are volatile and causes serious environmental damage.[1] To overcome these difficulties green technology initiates to search the solution.[2] They used solvent free alternate process when either one of the substrate is liquid used as the solvent for the reaction.[3] Most of the solvents are very crucial to the process so we should select a solvent which does not cause any impact on the health as well as environment[4] so some innovative and unconventional solvent must be used. Ionic liquids fulfill the requirement; it is used as catalyst as well as solvent. It is capable of changing their properties by changing the substitution on the nitrogen ring and also different anions.[5] It deserves, because of their favorable physico-chemical properties such as negligible vapourpressure, high thermal stability, large electrochemical window etc.[6-8]

The government and other regulatory bodies' role are to protect the environment from hazardous chemicals.[9] Water acts as green solvent has many advantages economically as well as synthetically like that ionic liquids acts as green solvent in many chemical reactions.[10] It is regarded as homogenous solvents[11] and properties as generally composed with chemical polar solvents. They defined as electrolytes composed entirely of ions at room temperature they are liquid.[12-13]

Ionic liquids can be synthesized by two methods 1.Direct neutralization 2.Metathesis method. In the first method imidazole combines with strong protic acids in the presence of toluene to form ionic liquid.[14] This method is simple to form ionic liquid due to the basic property of imidazole. The strong protic acid combines with base to form salt on heating HBr gas is released that will be abstracted by 1-alkyl imidazole to form ionic liquid. Two clear different layers obtained. It is washed with hexane and dried in vacuum Different 1- alkyl imidazolium based brønsted acidic ionic liquid can be prepared by using different alkali metal salts like KBF_4, KPF_6, $AgNO_3$ and AgBr etc.

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 1-propyl benzimidazole, 1-propylbenzimidazolium bromide, tertiary-butyl bromide, imidazole, acetic acid, glyoxal, and paraformaldehyde, Ammonium carbonate were purchased from SD fine chemicals, India and used are received. Ammonium tetraflouroborate, potassium

hexaflourophosphate, silver nitrate were purchased from Aldrich chemicals and used as received. 1-propyl benzimidazole was prepared by using chemical procedures.^{1}H 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 desolation temperature was set to 350^{0}C and the source temperature was set to 100^{0}C.the cone gas was set was set to a flow rate of 30.0L\Hr and the desolation gas flow was maintained at 626.0L\HR.

Synthesis of 1-propylbenzimidazolium based brønsted acidic ionic liquids.

Direct neutralization method

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

1. 1-propylbenzimidazolium triflate (BImnPHTA): Pale yellow color liquid, yield 92 %, ^{1}H NMR (DMSO-d_6, 400 MHz): 9.57 (s, 1H, 2-C*H*), 8.04 (d, 1H, 4C*H*), 7.86 (d, 1H, 7C*H*), 7.61 (m, 2H, 5,6CH), 4.44 (t, 2H, N-CH_2), 2.49 (m, 2H, CH_2), 0.90 (t, 3H, CH_3). ES-MS *m/z*: 161.2 $[M\text{-}CF_3SO_3]^+$.
2. 1-propylbenzimidazolium methanesulphonate (BImnPHMS): Pale yellow color liquid, yield 88 %, ^{1}H NMR (DMSO-d_6, 400 MHz): 9.61 (s, 1H, 2-C*H*), 8.04 (d, 1H, 4C*H*), 7.88 (d, 1H, 7C*H*), 7.59 (m, 2H, 5,6CH), 4.44 (t, 2H, N-CH_2), 1.90 (m, 2H, CH_2), 0.89 (t, 3H, CH_3), 2.34 (s, 3H, CH_3SO_3). ES-MS *m/z*: 161.2 $[M\text{-}CH_3SO_3]^+$.
3. 1-propylbenzimidazolium benzenesulfonate (BImnPHPS): Off white solid, yield 84 %, m.p 98°C. ^{1}H NMR (DMSO-d_6, 400 MHz): 9.62 (s, 1H, 2-C*H*), 8.04 (d, 1H, 4C*H*), 7.87 (d, 1H, 7C*H*), 7.60 (m, 2H, 5,6CH), 7.62 (2H, $C_6H_5SO_3$), 7.29 (3H, $C_6H_5SO_3$), 4.44 (t, 2H, N-CH_2), 1.90 (m, 2H, CH_2), 0.89 (t, 3H, CH_3). ES-MS *m/z*: 161.2 $[M\text{-}C_6H_5SO_3]^+$.

Metathesis method

Synthesis of 1-propylbenzimidazolium bromide.

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

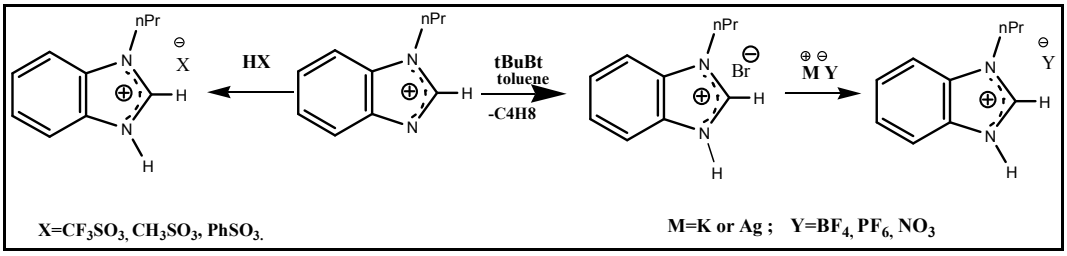
Metathesis followed by anion exchange method

15 mmol of ammonium tetrafluroborate or potassium hexaflurophosphate or silver nitrate was added to a solution of 15 mmol of 1-isopropylimidazolium bromide in (50 mL) CH_2Cl_2 / CH_3OH (5:1). The resulting mixture stirred for 3 hours at room temperature. The solution was filtered and the solvents were removed by vacuum.

1. 1-propylbenzimidazolium tetrafluroborate (BImnPHTFB): Off semi solid, yield 81%. ^{1}HNMR($CDCl_3$, 400 MHz): 9.52 (s, 1H, 2-C*H*), 8.01 (d, 1H, 4C*H*), 7.84 (d, 1H, 7C*H*), 7.56 (m,2H, 5,6CH), 4.43 (t, 2H, N-CH_2), 1.87 (m, 2H, CH_2), 0.89 (t, 3H, CH_3). ES-MS *m/z*: 161.2 $[M\text{-}BF_4]^+$
2. 1-propylbenzimidazoliume hexaflurophosphate (BImnPHHFP): Off white semisolid, yield 79%. ^{1}H NMR ($CDCl_3$, 400 MHz): 9.51 (s, 1H, 2-C*H*), 8.01 (d, 1H, 4C*H*), 7.84 (d, 1H, 7C*H*), 7.56 (m, 2H, 5,6CH), 4.42 (t, 2H, N-CH_2), 1.89 (m, 2H, CH_2), 0.89 (t, 3H, CH_3). ES-MS *m/z*: 161.2 $[M\text{-}PF_6]^+$
3. 1-propylbenzimidazolium nitrate (BImnPHN) : Off white solid, yield (83 %). M.p. 77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): 9.51 (s, 1H, 2-C*H*), 8.02 (d, 1H, 4C*H*), 7.84 (d, 1H, 7C*H*), 7.57 (m, 2H, 5,6CH), 4.42 (t, 2H, N-CH_2), 1.89 (m, 2H, CH_2), 0.89 (t, 3H, CH_3). ES-MS *m/z*: 161.2 $[M\text{-}NO_3]^+$

Results and discussion

We have performed experiments on toluene solution of 1-propylbenzimidazolium 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 hexane, toluene etc.



Scheme 1: Synthesis of 1-propylbenzimidazolium cation based brønsted acidic ionic liquids.

The investigated 1-propylbenzimidazolium bromide, 1-propylbenzimidazolium nitrate, 1-propylbenzimidazolium phenyl sulfonate are solids, 1-propylbenzimidazolium triflate,1-propylbenzimidazolium methane sulfonic acids are liquids, They have little vapor pressure. 1-propylbenzimidazolium tetrafluroborate, 1-propylbenzimidazolium hexaflurophosphate are semi solids. All the ionic liquids were characterized by H^1NMR and mass spectroscopy.

In the H^1NMR the 2-CH proton falls in the range of 9.51-9.62 ppm, the 4-CH proton ranges from 8.01-8.04 ppm. The 5-CH proton value is 7.56-7.61, the chemical shift value of $PhSO_3^-$is high compared to other anions of the imidazole. The value of $CH_3SO_3^-$ is just below of the $PhSO_3^-$ then for 4-CH proton the value of $PhSO_3^-$ is 8.04 for $CH_3SO_3^-$ the value is 8.01 ppm. The chemical shift value for 2-CH proton for nitrate and hexaflurophosphate are same with 9.51 ppm. Moreover the positive ion gave the corresponding cationic ($[M-X]^+$ peak falls in the range of 161.2 for all the all 1-propylbenzimidazolium cations The increasing order of acidity of ionic liquids were based on chemical shift of 2-CH H^1NMR

1-propylbenzimidazolium phenyl sulfonate > 1-propylbenzimidazolium methane sulfonate > 1-propylbenzimidazolium triflate.> 1-propylbenzimidazolium tetrafluroborate> 1-propylbenzimidazolium nitrate= 1-propylbenzimidazolium hexaflurophosphate.

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

Ionic liquids	^{1}H-NMR Value (ppm)			ESI-MASS (M/Z)
	2-CH	*4-CH*	5-CH	
BImnPHTA	9.57	8.04	7.61	161.2
BImnPHMS	9.61	7.88	7.59	161.2
BImnPHPS	9.62	8.04	7.60	161.2
BImnPHTFB	9.52	8.01	7.56	161.2
BImnPHHFP	9.51	8.01	7.56	161.2
BImnPHN	9.51	8.02	7.57	161.2

Conclusion

In conclusion we have synthesised and characterised six different examples of 1-propyl benz imidazolium based ionic liquids with different counter anionic substituents by simple neutralisation and metathesis method. Their H^1NMR and mass and physical nature also their comparison of diferent protons also reported in this paper.

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