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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF PROTIC IONIC LIQUIDS WITH IMIDAZOLIUM CATION

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Abstract

Ionic liquids have been recognized as “designer-solvents”. To optimize the use of ILs and design the desirable ILs, knowledge of the physical and chemical properties of ILs is essentially important. Several Protic ionic liquids (a sub class of ILs) containing imidazolium based cation are synthesized by the process of proton transfer from hydroxy acids (Bronsted acids) to substituted imidazole (Bronsted base) and their properties like solubility, refractive index, polarity, ionicity, viscosity, density and ionic conductivity are characterized. All imidazolium based room temperature protic ionic liquids studied here have a high ionic conductivity and good solubility etc.

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1. INTRODUCTION

Utilizing ILs is one of the goals of green chemistry because they create a cleaner and more sustainable chemistry and are receiving increasing interest as environmental friendly solvents for many synthetic and catalytic processes. Ionic liquids have unique and fascinating properties providing a remarkable opportunity for new science and technology⁽¹⁻⁷⁾. Ionic liquids (ILs) are salts that are liquid at or near room temperature. They are completely composed of ions and therefore have many potential applications. Recently, Ionic liquids have been also widely investigated for a variety of applications⁽⁸⁻¹²⁾. Subsets of ILs are protic ionic liquids (PILs), which are easily produced through the combination of a Brønsted acid and Brønsted base. The key properties that distinguish PILs from other ILs is the proton transfer from the acid to the base, leading to the presence of proton-donor and -acceptor sites, which can be used to build up a hydrogen-bonded network. The cations most commonly used in PILs are including primary, secondary, or tertiary ammonium ions, mono- or di-imidazolium ions, caprolactam, and guanidinium ions. The imidazolium and other heterocyclic rings can contain substituents on any of the carbons in the ring, so long as the nitrogen containing the positive charge retains a proton. A large variety of anions have been coupled with these cations were including organic (such as carboxylates), inorganic (such as nitrate or hydrogen sulfate), or fluorinated (such as bis (trifluoromethanesulfonyl) imide (TFSI), trifluoroacetic acid (TFA), and bis (perfluoroethylsulfonyl) imide (BETI), tetrafluoroborate, or hexafluorophosphate).

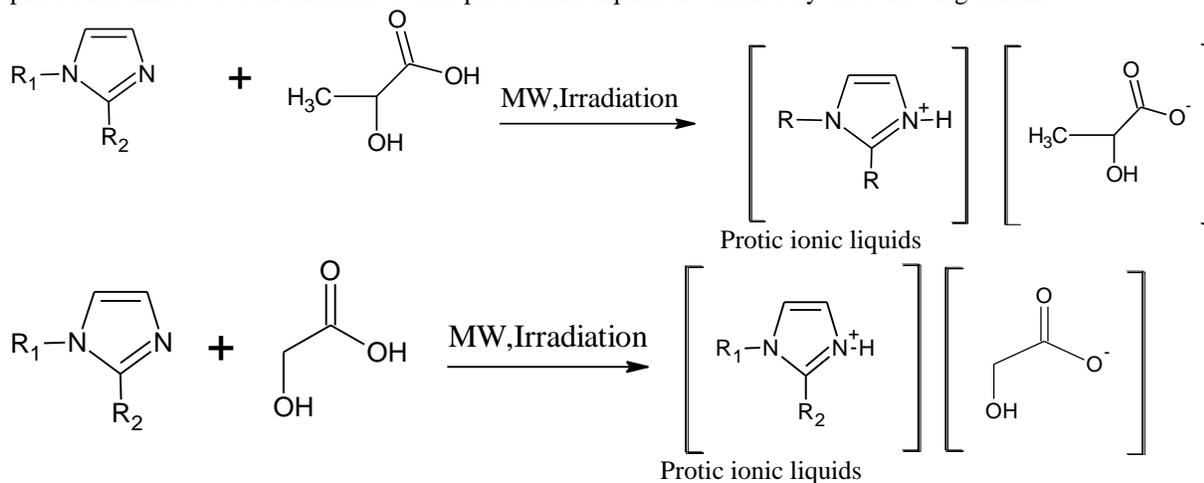
PILs can function as proton conducting material under non-humidified condition and can be employed as an electrolyte for non-humidified fuel cell⁽¹³⁾. Furthermore, the protic ionic liquids have been used as acidic catalysts for the Friedel Craft reaction, esterification⁽¹⁴⁾, protection reaction of aldehyde carbonyls⁽¹⁵⁾, Mannich reaction⁽¹⁶⁾, Biginelli condensation⁽¹⁷⁾ and Friedlander annulations⁽¹⁸⁾.

2. MATERIALS AND METHODS

2.1 EXPERIMENTAL

2.1.1 MICROWAVE SYNTHESIS OF PILs

The equimolar mixture of the precursor Bronsted acids (hydroxy carboxylic acids) and Bronsted bases (substituted imidazoles) were taken in a reacting vessel and stirred for an hour using magnetic stirrer and then it was placed in a microwave and irradiated. The protic ionic liquids are formed by the following scheme.



where R_1 -H, C_2H_5 - or C_4H_9 -. R_2 -H, CH_3

Table 1: Optimized reaction conditions for the synthesis of different branched protic ionic liquids using microwave irradiation

S.No	Bronsted bases	Bronsted acids	Protic Ionic liquids	MW power level(W)	Time (s)
1.	2-Methylimidazole	Lactic acid	[2MIML](colourless liquid)	160	30
2.	1-Ethylimidazole	Lactic acid	[1EIML](light yellow liquid)	080	40
3.	1-Butylimidazole	Lactic acid	[1BIML](yellow liquid)	240	20
4.	2-Methylimidazole	Glycolic acid	[2MIMG](colourless liquid)	160	40
5.	1-Ethylimidazole	Glycolic acid	[1EIMG](yellow liquid)	160	20
6.	1-Butylimidazole	Glycolic acid	[1BIMG](yellow liquid)	240	20

2.2 MEASUREMENT

The solubility of imidazolium based PILs was tested for various substances. The conductivity of the ionic liquid was systematically measured with an ELICO conductivity meter and a standard conductivity cell. Densities of ionic liquids were measured using Haursh's method. The viscosities of the ILs were measured using a Ostwald viscometer. For each IL, the experimental viscosity was obtained by averaging three to five flow time measurements. The refractive index of the ILs was measured using a commercial Spectrometer from Atago (model PAL-RI). The UV-visible spectra were recorded using Perkin Elmer Lambda35 Spectrometer and the FT-IR spectra were recorded using the Jasco (FT-IR 460) spectrometer. The proton nuclear magnetic resonance spectra were recorded in a Bruker 300 MHz NMR Spectrometer using CDCl_3 as solvent and the GC-MS were recorded using the JEOL GC MATE-II data system with maximum resolution of 6000.

3. RESULTS AND DISCUSSION

3.1 Characterization of the synthesized PILs

The structure of the synthesized PILs were confirmed by UV, FT-IR, ^1H NMR and GC-MS Spectral studies and the data were given below and the spectra were given in fig.1-24

2-Methylimidazoliumlactate

λ_{max} -233nm. IR-3426 cm^{-1} (N-H⁺), 1589 cm^{-1} (lactateion), 1417(lactateion), 1122 cm^{-1} (ringdeform). NMR chemical shift (δ) values: 8.05(1H(N-H in im)), 6.9(1H.im-H,s), 7.29(N-H⁺), 2.48(C-CH₃,3H,d), 1.48(m,-CH₃ in lactate), 4.04(-CH in lactate), 1.94(-CH(OH)COO-in lactate). m/z values: 171.29, 170.09, 81.29.

1-Ethylimidazoliumlactate

λ_{max} -228nm. IR-3444 cm^{-1} (N-H⁺), 1599 cm^{-1} (lactateion), 1393(lactateion), 1152 cm^{-1} (ringdeform). NMR chemical shift (δ) values: 7.6(1H.im-H,s), 7.28(N-H⁺), 3.875(-CH₂,2H,q), 0.903(CH₃,3H,t), 6.88(1H,d), 7.02(1H,d), 1.397(-CH₃,3H,m,d,in lactateion), 3.92 (-CH,1H,q, in lactate), 4.15(-CH in lactate) 1.755(-CH(OH) in lactate), m/z values - 185.03, 184.23, 95.23.

1-Butylimidazoliumlactate

λ_{max} -236nm. IR-3413 cm^{-1} (N-H⁺), 1594 cm^{-1} (lactateion), 1458 (lactateion), 1149 cm^{-1} (ring deform). NMR chemical shift(δ) values: 7.25(1H.im-H,s), 7.29(N-H⁺), 4.226(-CH₂,2H,q), 1.8(-CH₂,2H,m), 1.2(CH₂,2H,m), 0.921(-CH₃,3H,t), 7.026(1H,d), 7.25(1H,d), 6.990(1H,im,m), 1.427(-CH₃,3H,m,d in lactateion), 4.26(-CH, 1H,q,in lactate), 4.025(-CH(OH)in lactate), 1.56(CH(COO⁻),1H,s). m/z values-.213.21, 211.98, 123.21.

2-Methylimidazoliumglycolate

λ_{max} -232nm. IR-3432 cm^{-1} (N-H⁺), 1599 cm^{-1} (glycolateion), 1418(glycolateion), 1169 cm^{-1} (ringdeform). NMR chemical shift (δ) values: 8.15(1H(N-H in im)) 6.893 (1H.im-H,s), 7.1(N-H⁺), 2.38(C-CH₃,3H,d), 3.96(m,-CH₂ in glycolate), 2.16(CH(COO⁻) in glycolate). m/z values - 158.91, 157.91, 82.77.

1-Ethylimidazoliumglycolate

λ_{max} -237nm. IR-3424 cm^{-1} (N-H⁺), 1598 cm^{-1} (glycolateion), 1418(glycolateion), 1160 cm^{-1} (ringdeform). NMR chemical shift(δ) values: 7.626(1H.im-H,s), 7.3(N-H⁺), 3.86(-CH₂,2H,q), 1.19(-CH₃,3H,t), 6.89(1H,d), 7.038(1H,d), 3.96(m,-CH₂in glycolate), 2.16(-CH₂(COO⁻) in glycolate) m/z values-171.49, 170.28, 95.26.

1-Butylimidazoliumglycolate

λ_{max} —240nm. IR-3416 cm^{-1} (N-H⁺), 1598 cm^{-1} (glycolateion), 1408(glycolateion), 1169 cm^{-1} (ring deform) .NMR chemical shift (δ) values: 7.209 (1H.im-H,s), 7.215(N-H⁺), 4.13(-CH₂,2H,q), 1.769(-CH₂,2H,m), 1.208(CH₂,2H,m), 0.916(-CH₃,3H,t), 6.883(1H,m), 7.065(1H,d), 3.94(-CH₂(OH), 2H,s in glycolate ion), m/z values-204.91, 203.79, 128.72

Fig.1-UV Spectrum of PIL1

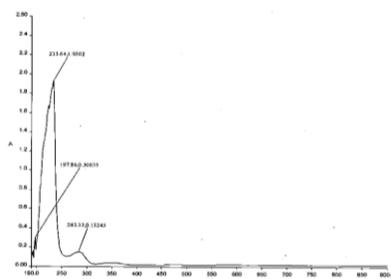


Fig.2-UV Spectrum of PIL2

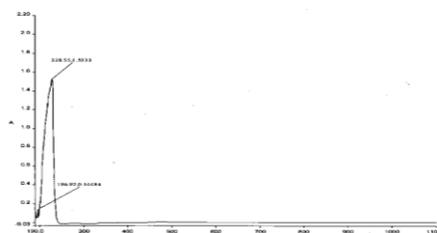


Fig.3-UV Spectrum of PIL3

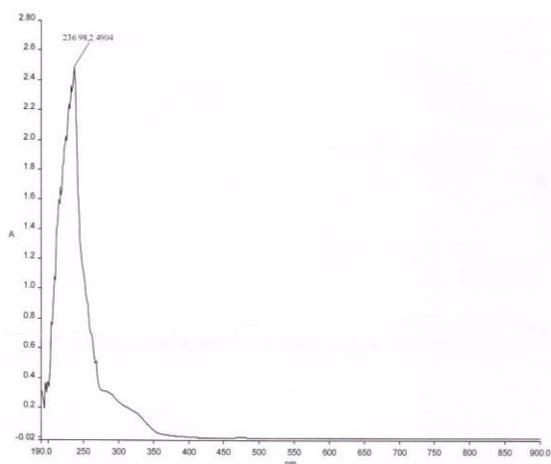


Fig4-UV Spectrum of PIL4

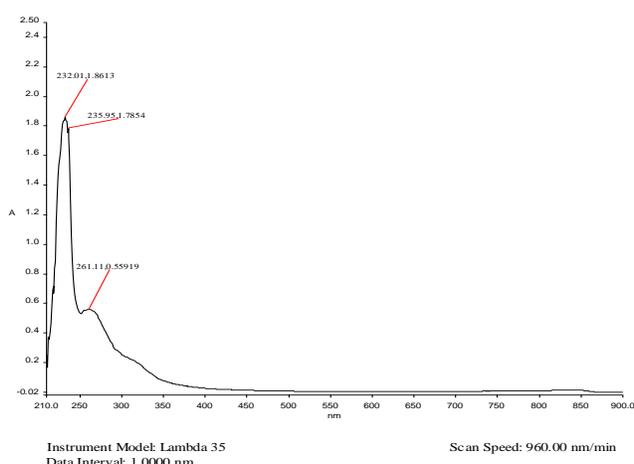


Fig.5-UV Spectrum of PIL5

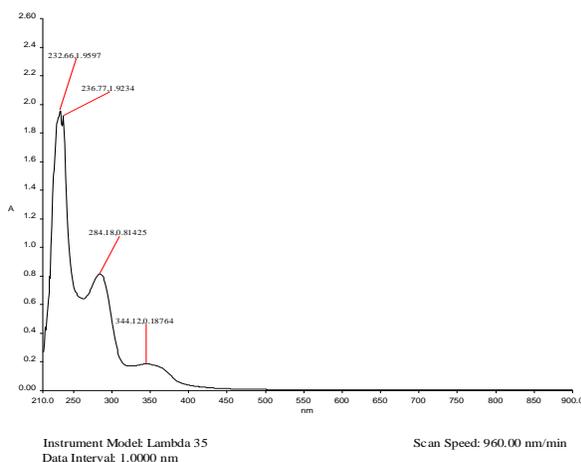


Fig.6-UV Spectrum of PIL6

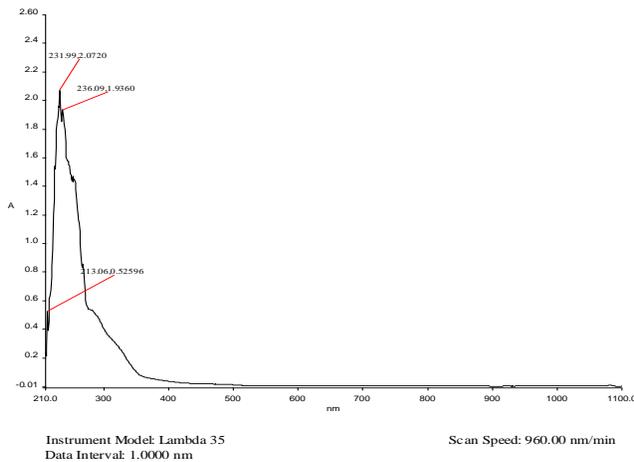


Fig.7-IR Spectrum of PIL1

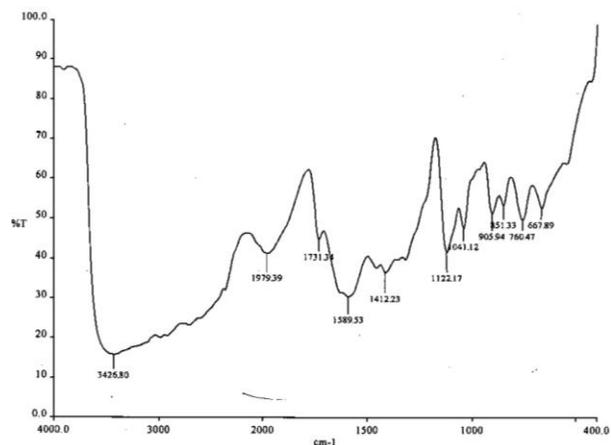


Fig.8-IR Spectrum of PIL2

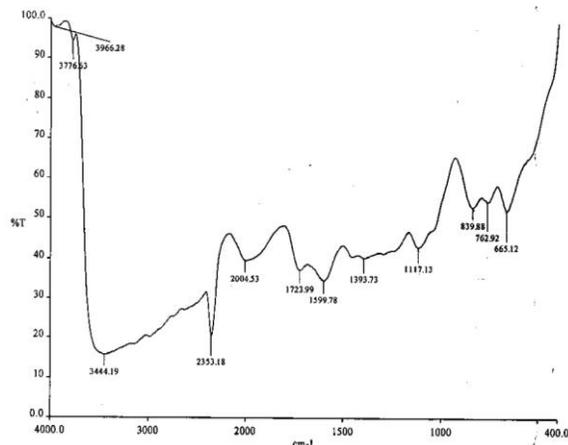


Fig.9-IR Spectrum of PIL3

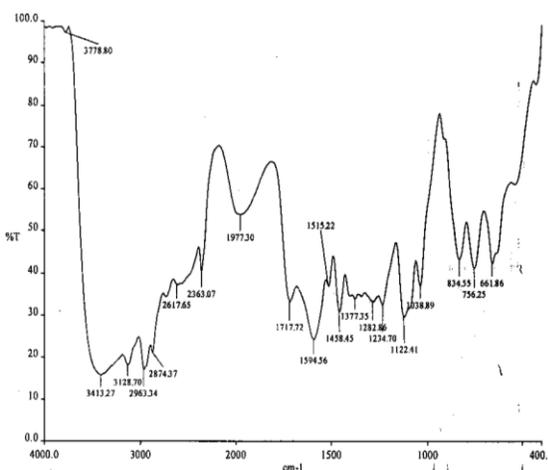


Fig.11-IR Spectrum of PIL5

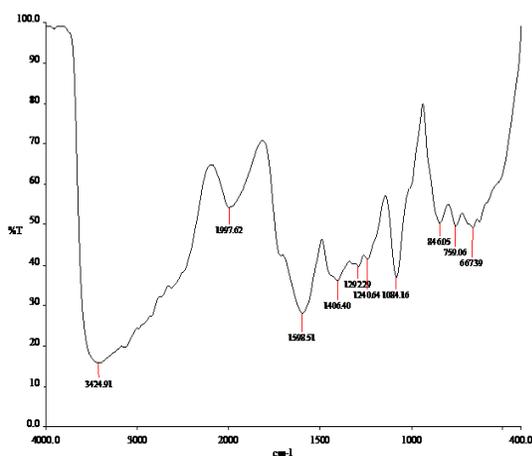


Fig13-NMR Spectrum of PIL1

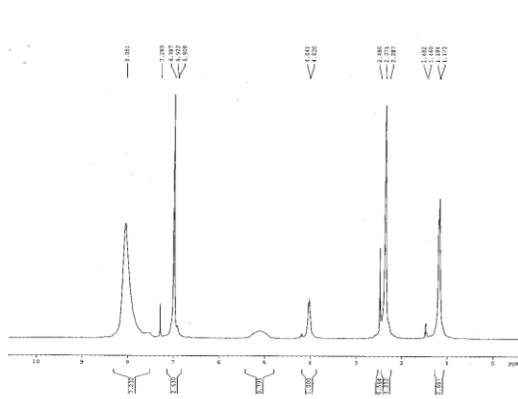


Fig.10-IR Spectrum of PIL4

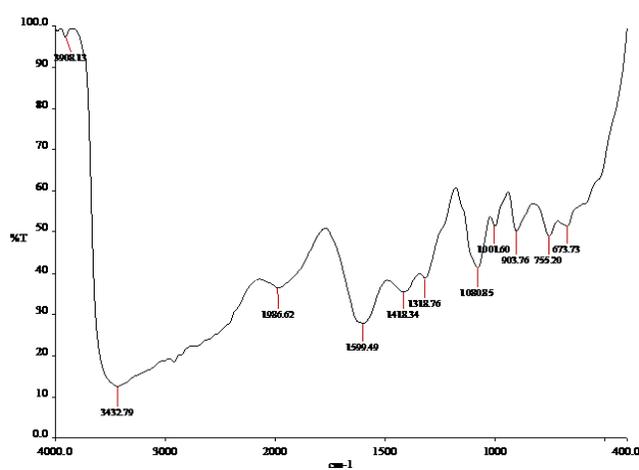


Fig.12-IR Spectrum of PIL6

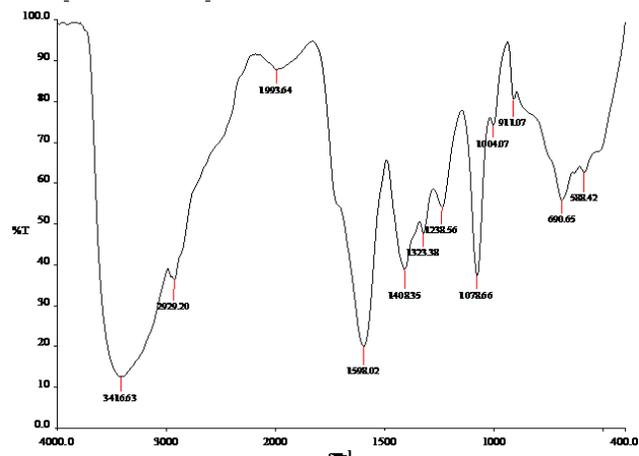


Fig14-NMR Spectrum of PIL2

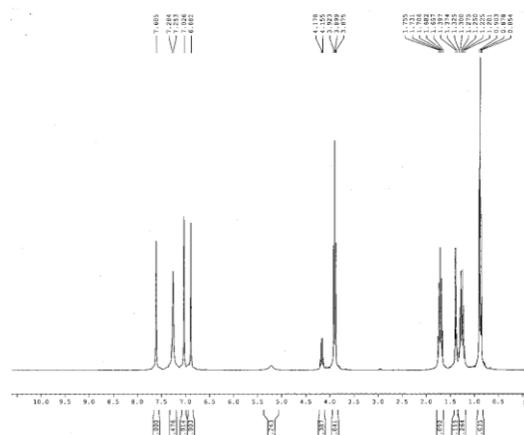


Fig19-Mass Spectrum of PIL1

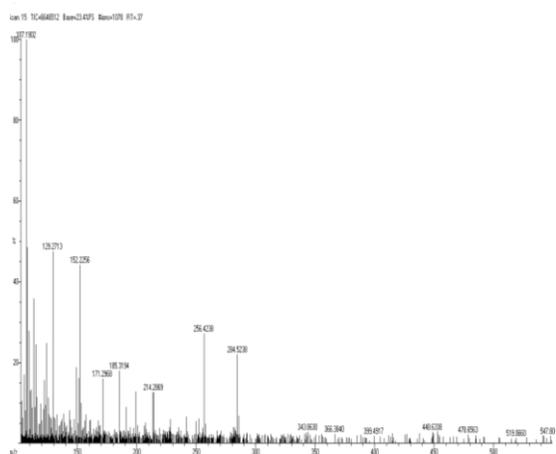


Fig20-Mass Spectrum of PIL2

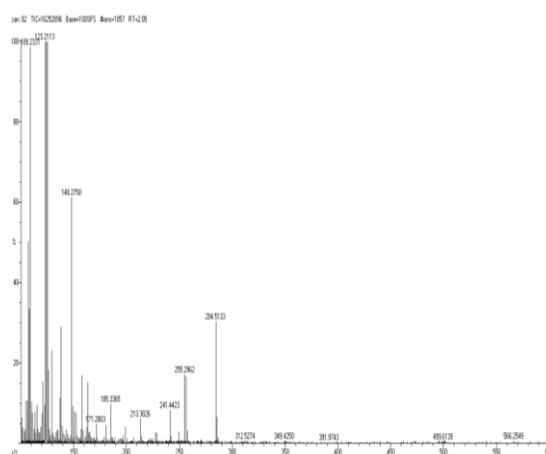


Fig21-NMR Spectrum of PIL3

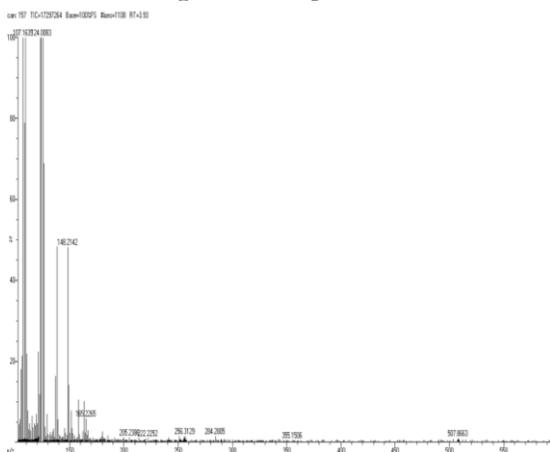


Fig22-NMR Spectrum of PIL4

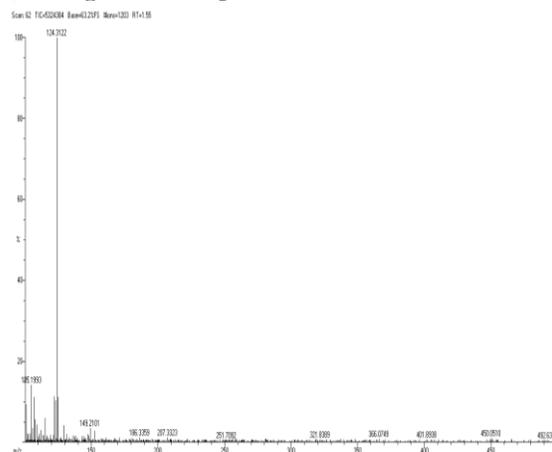


Fig23-NMR Spectrum of PIL5

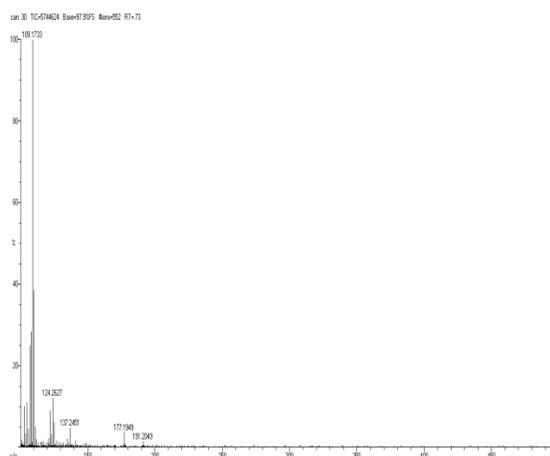
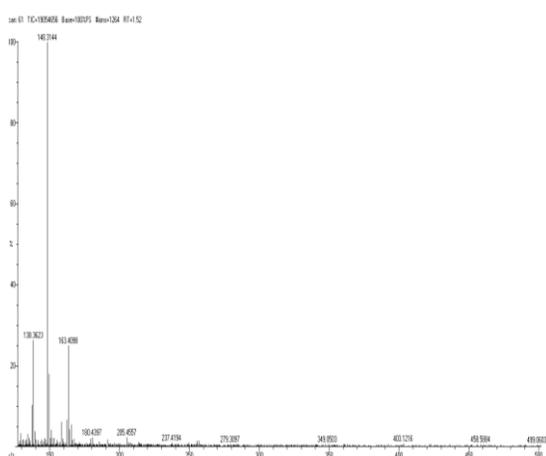


Fig24-NMR Spectrum of PIL6



3.2 Solubility

To find out the solubility, the above prepared PILs are tested for the following substrate like benzophenone, diphenylamine, p-bromoacetanilide, 4-hydroxybenzoic acid, benzanilide, p-nitroacetanilide, sulphanic acid, hydroquinone, β -naphthol, α -naphthol, o-phenylindiamine, picric acid, naphthalene, benzidine, resorcinol, biphenyl, hydroquinone, hydrazinedihydrochloride, 8-hydroxyquinoline, p-nitrophenol, glycine, 2-hydroxy benzaldehyde, p-chlorobenzaldehyde and show good solubility.

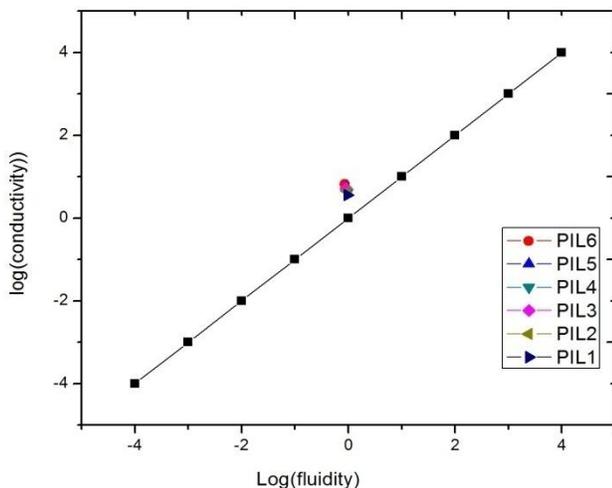
Table 2 . Various Physical properties of PILs

S.No	Protic Ionic liquids	Conductance Sm^{-1}	Viscosity g/cm^{-3}	Density cP	Refractive index	ΔpKa
1.	2-Methylimidazoliumlactate	6.64	1.1725	1158	1.4243	3.84
2.	1-Ethylimidazoliumlactate	5.51	1.0908	1193	1.4562	3.43
3.	1-Butylimidazoliumlactate	4.15	1.0503	1236	1.4922	3.23
4.	2-Methylimidazoliumglycolate	5.29	1.1023	1105	1.3962	3.92
5.	1-Ethylimidazoliumglycolate	4.49	1.0676	1178	1.4773	3.46
6.	1-Butylimidazoliumglycolate	3.61	1.0336	1216	1.4921	3.26

3.3. Ionicity

Ideally in PILs, the proton transfer is complete from the acid to the base, such that the only individual species present are the resulting cation and anion. In reality, this is unlikely since the proton transfer may be less than complete, resulting in the neutral acid and base species being present, and aggregation and association of either ions or neutral species can occur. The Walden plot of the $\log(\text{equivalent conductivity})$ versus $\log(\text{fluidity})$ can be used to show how good an ionic liquid is. From The Walden plot, it was noted that all the points were fall above the standard line (plot of the $\log(\text{equivalent conductivity})$ versus $\log(\text{fluidity})$ for KCl) which show that all the synthesized PILs having good ionicity (Fig 25). In the second method, the aqueous pKa values for the precursor acids and bases have been employed to calculate ΔpKa which was used to estimate the completion of the proton transfer. A large ΔpKa ($\text{pKa}(\text{base}) - \text{pKa}(\text{acid})$) is suggestive of good proton transfer. The ΔpKa for all PILs were reported in table 2. From those values it was clear that, all the PILs were formed with good proton transfer.

Fig.3 Walden Plot



3.4. Density

The density values for all PILs have been reported are given in Table 2. The density of a material depends on how closely the ions can pack together and, hence, on the size and shape of the ions and ion-ion interactions. It is apparent that the density decreases slowly as the alkyl chain length increases for alkyimidazolium cations, or alkylcarboxylate anions.

3.5. Refractive Index and Molar Refractivity

The density values for all PILs have been reported are given in Table 3. The refractive index, n_D , of a material can give a measure of its polarity, and the molar refractivity, MR, is directly related to the polarizability of the material.

3.6. Viscosity

The viscosity values for all PILs have been reported are given in Table 3. The viscosity is dependent on the ion-ion interactions, such as Vander waals interactions and hydrogen bonding, with greater interactions leading to higher viscosities. The viscosity increases slowly as the alkyl chain length increases for alkyimidazolium cations, or alkylcarboxylate anions.

3.7. Ionic Conductivity

The ionic conductivity is governed by the mobility of the ions, which depends on the viscosity and the number of charge carriers, which in turn depend on the molecular weight, density and ion sizes. Any ion association will cause a decrease in the ionic conductivity through decreasing the number of available diffusible ions for the aggregation numbers of PILs). Consequently, PILs with more delocalized charges and fewer ion interactions will have higher conductivities. The ionic conductivities were well-reported for the PILs, and the values are given in Table 3. The conductivity for PILs with alkyl ammonium and alkyimidazolium cations decreased as the alkyl chain length increased, with the greatest change for short chains (C1-C4) and little change for longer chains (C4-C12).

4. CONCLUSION

Six PILs containing substituted imidazolium cation and hydroxyl carboxylate anion were designed and synthesized by the proton transfer process. The so formed PILs were confirmed by the spectral analysis. Their physical properties like solubility, density, viscosity, refractive index, ionicity and ionic conductivity were also measured by the appropriate techniques. Many organic substances which were insoluble in water could be soluble in all the PILs. This showed that all the PILs were good solvent and could be used as a solvent for much organic and inorganic synthesis. All the PILs had good ionic conductance and thus having characteristic electrolytic properties and they could be used as electrolytes for electroplating and electrodeposition.

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