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Authors: Mzukisi Matandabuzo and Peter A. Ajibade

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Synthesis, characterization, and physicochemical properties of hydrophobic pyridinium-based ionic liquids with N-propyl and N-isopropyl

Mzukisi Matandabuzo, Peter A. Ajibade*

School of Chemistry & Physics, College of Agriculture, Engineering & Science, University of

KwaZulu- Natal, P/Bag X01, Scottsville 3209, Pietermaritzburg, South Africa

Abstract

In this study, synthesis and physicochemical properties of four pyridinium-based ionic liquids (ILs): *N*-propylpyridinium bromide [*N*-propylPyr]⁺[Br]⁻, *N*-isopropylpyridinium bromide [*N*-isopropylPyr]⁺[Br]⁻, *N*-propylpyridinium hexafluorophosphate [*N*-propylPyr]⁺[PF₆]⁻, and *N*-isopropylpyridinium hexafluorophosphate [*N*-isopropylPyr]⁺[PF₆]⁻ are reported. The molecular structures of these compounds were characterized by FT-IR, ¹H, ¹⁹F, and ³¹P-NMR, spectroscopy. The thermal properties, conductivity, and solubility of these ionic liquids were also investigated. The effects of propyl and isopropyl alkyl lateral chain at the N-position of pyridinium cation on the thermal stability, conductivity, and solubility of ionic liquids are discussed. The results obtained confirmed that the ionic liquids based on pyridinium cations exhibit higher decomposition temperature, low melting points, immiscible with water, and their conductivities are mainly influenced by mobility of ions.

Keywords: Ionic liquids; pyridinium cation; hexafluorophosphate; thermal stability; conductivity; solubility in water.

*Corresponding author email: ajibadep@ukzn.ac.za

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1 Introduction

Ionic liquids (ILs) are salts (organic and/or inorganic), with melting point relatively lower than (<100°C) and are liquid at room temperature. ^[1-2] They were first discovered in 1914, when Weldon reported the physical properties of ethyl ammonium nitrate (C₂H₅NH₃)NO₃ with melting point of 12°C.^[2] Ionic liquids consist of an organic cation with delocalised charge, and organic or inorganic anion (known as counter-ion).^[3-4] The tunability of ionic liquids to give specific properties for a particular application is the reason for being given nickname "designer solvents". ^[1-5] Ionic liquid salts possess special properties such as relatively non-volatile ^[6], good thermally stability ^[7], low melting point ^[6, 8], and high density. ^[9] Some of the properties of ionic liquids largely depend on the chosen cation and/or alkyl chain, and anion. ^[10-11] For instance, Kubisa ^[1] reported that both the cation and anion contribute to the melting point of an ionic liquid. An ionic liquid salt has no measurable vapour pressure, which makes them good replacements for volatile organic solvents.^[12] Literature has also reported that organic cation(s) with low symmetry or branched chain relatively produce low melting point salts. ^[13] Hydrophobicity, viscosity, density, and solvation of ionic liquids can be changed or manipulated by changing the anion. ^[14-15]

The common procedure used to synthesize water-immiscible ILs involves the preparation of aqueous solution of halide salt with the desired cation (i.e. 1-ethly-3-methylimmidazolium halide),

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followed by the anion-exchange process. ^[16, 18] The water solubility or miscibility of ionic liquids usually depends on the type of counter-ion used. ^[15, 17] A typical example is that of 1-butyl-3methylimidazolium, whereby the ionic liquid of 1-butyl-3-methylimidazolium cation and PF₆⁻ anion is immiscible in water, whereas that of 1-butyl-3-methlyimmidazolium cation and BF₄⁻ is soluble. ^[15] The functionality of ionic liquids is tunable by adjusting or functionalising the molecular structure of both the organic cation and anion. ^[16, 19] Originally, ionic liquids were associated with green chemistry as substitutes of volatile and flammable solvents. However, these types of salt have recently drawn a significant interest and application in organic and polymer analytical nanotechnology, chemistry, catalysis, electrochemistry, chemistry, energy, micellization, and biotechnology.^[20-23] They are also used as plasticizers, additives, components of polymer electrolytes, and porogenic agents to polymers ^[23]. Besides, there is very limited report on the application of ionic liquids for wastewater treatment and for acid mine drainage remediation.

There are some reports of ionic liquids containing pyridinium cation in the literature. ^[24-27] Papaiconomou *et al.* ^[24] synthesized and studied the physicochemical properties of four pyridinium-based ionic liquids namely: 1-butyl-4-methylpyridnium bis(trifluoromethylsulfonyl) imide [MBPYR]⁺[Tf₂N]⁻, 1-butyl-4-methylpyridnium trifluoromethyl sulfonate [MBPYR]⁺[TfO]⁻

, 1-butyl-4-methylpyridnium nonafluorobutyl sulfonate [MBPYR]⁺[NfO]⁻, and 1-butyl-4methylpyridnium dicyanamide [MBPYR]⁺[Br]⁻, respectively. They discovered that two of the four pyridinium-based ionic liquids, [MBPYR]⁺[Br]⁻ and [MBPYR]⁺[NfO]⁻ were solid at room temperature, while [MBPYR]⁺[Tf₂N]⁻ and [MBPYR]⁺[TfO]⁻ were found to have densities higher than that of water at ambient temperature, which were 1.35 and 1.17 g·mL⁻¹, respectively. Again, [MBPYR]⁺[NfO]⁻ and [MBPYR]⁺[Tf₂N]⁻ were found to be insoluble in water at 25°C. The melting points obtained for these four ionic liquids followed this increasing order: [MBPYR]⁺[Br]⁻ > [MBPYR]⁺[NfO]⁻ > [MBPYR]⁺[TfO]⁻ >> [MBPYR]⁺[Tf₂N]⁻. They concluded that ionic liquids containing 1-butyl-4-methylpyridinium cations have considerable high melting points, high densities, but lower solubility's in water than their imidazolium cation counterparts.^[24-25]

Dzyuba^[26] reported the synthesis of N-substituted pyridinium bromide ionic liquids. Although the research and synthesis of pyridinium-based ionic liquids is gaining momentum and recognition lately, the wide applicability of imidazolium–based ionic liquids makes the pyridinium-containing ionic liquids less attractive. N-substituted pyridinium halides are known to be solids, which is in agreement with the findings of Papaiconomou and co-workers ^[24]. Dyzuba ^[26] also reported the novel synthesis of dicationic salts containing both pyridinium and ammonium cations. Herein, we report the synthesis, characterization, and physicochemical properties of four hydrophobic

pyridinium–based ionic liquids with hexafluorophosphate inorganic counter anion and threecarbon isomeric alkyl chain lateral attached to the N-position of the pyridinium cation. To the best of our knowledge, no one has reported the synthesis, characterization, and physicochemical properties of pyridinium-based ionic liquids based on comparison of three carbons isomeric alkyl groups (propyl or isopropyl) at the N-position of pyridinium cation.

2 Experimental Sections

2.1 Materials and Chemicals

All chemicals were obtained from Sigma-Aldrich or Merck and were used as received without further purification unless stated otherwise. 1-bromopropane (99%), 2-bromopropane (99%), pyridine (\geq 99.0%), dimethyl sulfoxide (\geq 99.9%), dimethyl formamide (\geq 99.8%), Toluene (\leq 99%), dichloromethane (\geq 99.9%), and potassium hexafluorophosphate (\geq 99%). The ionic liquids: Npropylpyridinium $[N-\text{propylPyr}]^+[\text{Br}]^-$, *N*-isopropylpyridinium [Nbromide bromide isopropylPyr]⁺[Br]⁻, *N*-propylpyridinium hexafluorophosphate $[N-\text{propylPyr}]^+[\text{PF}_6]^-$, *N*isopropylpyridinium hexafluorophosphate [N-isopropylPyr]⁺[PF₆]⁻ were synthesized based on literature method. [10, 24, 26-27]

2.2 Synthesis of ionic liquids (ILs)

Four ionic liquids were synthesized as shown in Scheme 1. The synthesized ionic liquids contain pyridinium cation and either halide or hexafluorophosphate as counter anion. These ionic liquids were synthesized via two-step metathesis method that involves the quaternization of pyridine with three-carbon alkyl bromide, followed by ion exchange with potassium hexafluorophosphate (KPF₆), as detailed below.



Scheme 1 General synthetic route of ionic liquids.

Synthesis of N-alkylpyridinium bromide: Into a vigorously stirred solution of pyridine (4.21 mL, 52.10 mmol) and 20 mL toluene at 0°C, 1-bromopropane (4.09 mL, 45.0 mmol) or 2-bromopropane (4.91 mL, 45.0 mmol) was added slowly in three-neck round bottom flask. The mixture was heated to reflux at 100°C for 24 hours. Toluene was decanted and the remaining brown to gold viscous liquid was re-crystallized in dichloromethane twice. Dichloromethane was evaporated using vacuum rotary evaporator and the product was dried in an oven at 70°C for 10

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hours to further remove any solvent residue. The product obtained was either N-propylpyridinium

bromide [*N*-propylPyr]⁺[Br], or *N*-isopropyl pyridinium bromide [*N*-isopropylPyr]⁺[Br]⁻.

[N-propylPyr]⁺[Br]⁺: ¹H NMR (400 MHz, ppm, DMSO-*d*⁶, δ): 9.27-9.26 (2H, d, pyr-CH_o), 8.19-8.16 (2H, t, pyr-CH_m), 8.66-8.62 (1H, t, pyr-CH_p), 4.69-4.66 (2H, d, CH₂), 1.95-1.87 (2H, m, CH₂), 0.83-0.78 (3H, t, CH₃).

FT-IR (v/cm⁻¹): 3348 (=C-H, w), 2870 (C-H_{sp}³, s), 1591 (C=C_{pyr}, s), 1417 (C=N_{pyr}, m), 1145 (C-N, m).

[N-isopropylPyr]⁺*[Br]*⁺: ¹H NMR (400 MHz, ppm, DMSO-*d*⁶): 9.21- 9.22 (2H, d, pyr-CH_o), 8.62 -8.58 (1H, m, pyr-CH_p), 8.17- 8.13 (2H, t, pyr-CH_m), 5.08- 5.04 (1H, m, CH), 1. 62- 1.59 (6H, d, CH₃x2).

FT-IR (v/cm⁻¹): 3374 (=C-H, s), 3150-3109 (C-H_{sp}², s), 3091-2978 (C-H_{sp}³, s), 1635 (C=C_{pyr}, m), 1456 (C=N_{pyr}, m), 1157-1110 (C-N, m).

Synthesis of N-alkylpyridinium hexafluorophosphate: Viscous liquid of either [*N*-propylPyr]⁺[Br]⁻ or [*N*-isopropylPyr]⁺[Br]⁻ (1.0 mL), and 2.02 g (11 mmol) of potassium hexafluorophosphate salt were mixed in a 100-mL round-bottomed flask containing 10 mL of water and stirred for 12 hours at 50°C. The resultant product was re-crystallized from dichloromethane (2 x 10 mL) and dried with anhydrous magnesium sulphate to remove water residue. The solvent was evaporated by vacuum rotary evaporator at 40°C. Light brown to gold and white solid products were obtained and further dried at 70°C for 2 hours in an oven. It was observed that the obtained products have a tendency to melt and become liquids when stored in an

oven, although when stored in a fume hood at room temperature they tend to crystallized

immediately.

[N-propylPyr]⁺*[PF₆]*⁺: ¹H NMR (400 MHz, ppm, DMSO-*d*⁶, δ): 9.07- 9.06 (2H, d, pyr-CHo), 8.62- 8.58 (1H, t, pyr-CH_p), 8.17- 8.13 (2H, t, pyr-CH_m), 4.58- 4.55 (2H, t, CH₂), 1.99-1.90 (2H, m, CH₂), 0.90- 0.86 (3H, t, CH₃).

³¹**P NMR** (DMSO- d^6 , δ): -144.179 ppm (m, PF₆⁻, ${}^{I}J_{p-f} = 709.24$ Hz). ¹⁹**F NMR** (DMSO- d^6 , δ): - 69.240 to -71.129 ppm (d, PF₆⁻).

FT-IR (v/cm⁻¹): 3348 (=C-H_{pyr}, m), 3104 (C-H_{sp}², s), 2978-2885 (C-H_{sp}³, s), 1640 (C=C_{pyr}, m), 1566-1409 (C=N_{pyr}, s), 1179 (C-N, s).

[N-isopropylPyr]⁺*[PF₆]*⁺: ¹H NMR (400 MHz, ppm, DMSO-*d*⁶, δ): 9.17- 9.15 (2H, d, pyr-CH₀), 8.61 -8.57 (1H, m, pyr-CH_p), 8.17- 8.13 (2H, t, pyr-CH_m), 5.03- 5.01 (1H, m, CH), 1.62 – 1.61 (6H, d, CH₃x2).

³¹**P** NMR (DMSO- d^6 , δ): -131.54 to -157.32 ppm (m, PF₆⁻, ¹ $J_{p-f} = 713.09$ Hz). ¹⁹**F** NMR (DMSO- d^6 , δ): -69.25 to -71.13 ppm (d, PF₆⁻).

FT-IR (v/cm⁻¹): 3336 (=C-H_{pyr}, m), 3150-3109 (C-H_{sp}², m), 2907 (C-H_{sp}³, m), 1635 (C=C_{pyr}, s), 1486 (C=N_{pyr}, s), 1156 (C-N).

2.3 Characterization techniques

FTIR spectral studies were carried out on (Perkin-Elmer, Universal ATR Sampling Accessory).

¹H, ³¹P, and ¹⁹F-NMR spectra were obtained in D₂O and DMSO- d^6 on a Bruker Avance III 400 at frequencies 500 MHz or 400 MHz (¹H). Thermal stability and glass transition temperature (T_g) of ionic liquids were determined by Perkin-Elmer thermo-gravimetric analyser (TGA 4000) and differential scanning calorimeter (DSC 4000). Samples (10-30 mg) for TGA were placed in a

ceramic sample pan and heated above a temperature range of 50-900°C at a heating rate of 40°C/min. For the total decomposition of carbon materials from the samples, gas was switched from nitrogen to air at 700°C. Samples in a DSC were heated within a temperature range of 25-250 °C at a heating rate of 20 °C/min for pyridinium ionic liquids with halide anion and 25-400°C for pyridinium ionic liquids with hexafluorophosphate anion. DSC runs were obtained under nitrogen gas flow. Conductivity of the ionic liquids was measured by JENWAY 4510 Conductivity meter in temperature range of 22-24°C. To test the solubility of the ionic liquids, the samples were dissolved in different aqueous and organic solvents. Again, they were dissolved in the mixture of methanol/water (80/20%), vigorously stirred and passed through solid phase extraction tube (SPE). The solutions collected from the SPE tank were analysed by liquid chromatography (Shimandu, LC-20AB, Prominance Liquid chromatography), using mixture of methanol/water (80/20) at a flow rate 1.0 mL/min.

3 Results and discussion

3.1 FTIR spectra studies

Four ionic liquids have been synthesized in this study, and their molecular structures, composition, and functional groups were determined by FTIR, ¹H, ³¹P, and ¹⁹F-NMR analyses. The FTIR spectra obtained for the ionic liquids in this study are presented as supplementary material **SI. 01**. In [*N*-

propylPyr]⁺[Br]⁻, the presence of a weak band around 3348 cm⁻¹ can be attributed to =C-H stretch for pyridinium in *ortho*, *meta*, and *para* positions. Strong vibrational bands at 2870 and 1579 cm⁻¹ ¹ can be categorically assigned to C-H_{sp}³ for propyl group, and C=C of pyridine, respectively. Medium peaks at 1417 and 1145 cm⁻¹ are due to the C=N of pyridinium cation and C-N between the nitrogen group of pyridinium and first carbon of propyl, respectively. For [*N*isopropylPyr]⁺[Br]⁻, although slightly shifted, but similar bands were observed. For ionic liquids containing PF₆⁻, vibrational bands were found to be similar to those obtained for ionic liquids containing bromide. These closely related observations confirmed that ion-exchange was carried out successfully and the cationic components of the ionic liquids were unaltered.

3.2 NMR spectra studies

¹H-NMR spectra of all the as-synthesized ionic liquids were obtained successfully and confirmed the purity of the compounds synthesized. For example, ¹H-NMR spectrum of [*N*-propylPyr]⁺[Br]⁻ (**SI.04A**) shows signals at 9.27-9.26, 8.19-8.16, and 8.66-8.62 ppm due to the protons resonance at *ortho-*, *meta-*, and *para-*positions of pyridinium ring. Signals at 4.94-4.66 and 1.95-1.87 ppm can be correctly assigned to the two -CH₂ consecutive groups of the propyl lateral chain, while the signals at 0.83-0.78 ppm are due to the methyl (-CH₃) group of propyl. As depicted in (**SI.04B**), relatively similar but less deshielded ¹H-NMR signals were obtained for [*N*-propylPyr]⁺[PF₆]⁻. For

isopropyl-featuring ionic liquids, [*N*-isopropylPyr]⁺[Br]⁻(**SI.02**), ¹H-NMR signals responsible for proton resonances at *ortho-*, *para-*, and *meta-*positions were observed at 9.22-9.21, 8.62-8.58, and 8.17-8.13 ppm, respectively. The multiplet at 5.08-5.04 ppm is due to the single-proton of the isopropyl carbon close to pyridinium-nitrogen atom. The doublet at 1.62-1.59 ppm is due to the six-protons of the two methyl groups (CH₃x2) of isopropyl. Again, the hydrophobic moiety of the [*N*-isopropylPyr]⁺[Br]⁻, that is, [*N*-isopropylPyr]⁺[PF₆]⁻ shows similar but comparable less deshielded proton signals. The presence of bromide ion in hydrophilic ionic liquids has resulted in some proton resonances being deshielded. It has been reported that the electron density of substituents in a compound usually affects peak/signal position in the ¹H-NMR. However, due to high electronegative behaviour of halogens, protons close or associated with halides are normally deshielded and appear at downfield.

Furthermore, ³¹P and ¹⁹F-NMR for both hydrophobic [*N*-propylPyr]⁺[PF₆]⁻ and [*N*-isopropylPyr]⁺[PF₆]⁻ ionic liquids containing PF₆⁻ counteranion are presented (supplementary **SI**. **02-05**). For [*N*-propylPyr]⁺[PF₆]⁻, ³¹P was found to have a multiplet (m) around -144.179 ppm, which confirmed the presence of phosphorous atom coupled with six fluorine atoms. ¹⁹F was found to have a doublet (d) around -169.25 to -71.13 ppm, confirming the coupling of six fluorine atoms with one phosphorous atom. The coupling distances between the peaks in both ³¹P and ¹⁹F

NMR spectra were found to be approximately the same and constituted the coupling constant of ${}^{1}J_{p-f} = 709.24$ Hz. For [N-isopropylPyr]⁺[PF₆]⁻, ${}^{31}P$ was found to have multiplet peaks around -131.54 ppm, while ¹⁹F was found to have doublet around -69.25 to -71.13 ppm and with coupling constant of ${}^{1}J_{p-f} = 713.09$ Hz. However, both ${}^{31}P$ and ${}^{19}F$ NMR confirmed the presence of fluorine and phosphorous atoms coupled together in the form of PF_{6} in the as-synthesized ionic liquids. The close range of the obtained coupling constants for both hydrophobic ionic liquids is the clear indication that the counter anion was successfully attached to the pyridinium counter cation in both ionic liquids and the synthetic method was successful. To further complement the FTIR, ¹H, ¹⁹F, and ³¹P-NMR results, single mass analysis data was collected. The accurate mass of the synthesized compounds based on C, H, and N is presented in (**S1.06 to S1.07**). Comparatively, it is established that the experimental accurate mass values (122.0973 and 122.0966 m/z for isopropyl pyridinium and propyl pyridinium, respectively) are in agreement with the calculated mass (122.10 m/z $C_8H_{12}N^+$). This therefore in combination with the results obtained from ¹H, ¹⁹F, and ³¹P-NMR confirmed the successful synthesis and absolute purity of the compounds.

3.3 Physicochemical Properties

3.3.1 Thermogravimetric analyses

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Thermogravimetric analysis (TGA) is usually used to obtain information about the thermal stability character of the synthesized ionic ILs. As shown in Fig. 1, pyridinium-based ionic liquids with halide counter anion, [*N*-propylPyr]⁺[Br]⁻ and [*N*-isopropylPyr]⁺[Br]⁻ displayed minor weight losses, less than 5% within 100°C which is due to the loss of moisture from the samples. Considerable weight loss between 18-35% was observed at temperatures above 290°C for both pyridinium ionic liquids with halide due to the decomposition of the ionic liquid salts. [*N*-propylPyr]⁺[Br]⁻ and [*N*-isopropylPyr]⁺[Br]⁻ were seen to be thermally stable below 400°C and their total decompositions were recorded at 356°C and 342°C, respectively, showing unimodal decomposition character.

[N-propylPyr]⁺[PF₆]⁻ and [N-isopropylPyr]⁺[PF₆]⁻, that is, hydrophobic pyridinium-based ILs with PF₆⁻ counter anion were observed to be thermally stable up to 400°C. Minor weight loss of about 8-17% responsible for moisture weight loss was seen at onset temperatures 301°C and 322°C for the two hydrophobic ionic liquids. Significantly decomposition between 400-550°C was observed for both hydrophobic ionic liquids. Contrarily, hydrophobic ionic liquids showed multimodal decomposition characteristics. Carbon loss for both [N-propylPyr]⁺[PF₆]⁻ and [N-isopropylPyr]⁺[PF₆]⁻ was also observed at 721°C and 789°C, respectively.

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Figure 1 TGA for pyridinium-based ionic liquids

It can therefore be concluded that ionic liquids with hydrophobic counter anion such as PF_6^- are more stable than those with halide counter anion (hydrophilic). Papaiconomou *et al.*^[24] also discovered that thermal stability of ionic liquids is related to the nature of the counteranion involved. For the ionic liquids investigated in this study, it was also evident that ILs with pyridinium cation containing isopropyl group on the N-position of pyridinium were more stable than those with propyl counterpart in the following order: [*N*-IsopropylPyr]⁺[Br]⁻[*N*propylPyr]⁺[Br]⁻, while [*N*-isopropylPyr]⁺[PF₆]>[*N*-propylPyr]⁺[PF₆]⁻ in terms of thermal stability. Thus, the thermal stability of ionic liquids in this study is in accordance with counter

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anions involved and the isomeric alkyl groups on the N-position of pyridinium in the following trend: $[N-isopropylPyr][PF_6] > [N-propylPyr][PF_6] > [N-IsopropylPyr][Br] > [N-propylPyr][Br].$

3.3.2 Melting point and Glass transition temperatures

Melting point and glass transition temperatures were obtained using differential scanning calorimetry (DSC). DSC runs were conducted under nitrogen gas flow and sample weight range 5-20 mg. Table 1 show the melting point (T_m) , glass transition (T_g) , decomposition (T_d) temperatures in degrees Celsius, and ionic conductivity (σ , mS) at given temperatures. Figs. 2 and 3 show the DSC thermograms of the ILs synthesized in this study. For instance, Fig. 2 show the transition Tg of [N-propylPyr]Br] at 28°C and that of [N-isopropylPyr][Br] at 25°C, that is, the inflation point (endothermic direction) between the first peak onset temperature and offset temperature, respectively. Glass transitions of hydrophobic $[N-propy|Pyr][PF_6]$ and $[N-propy|Pyr][PF_6]$ isopropylPyr][PF₆] ILs were observed to be slightly smaller in comparison to other corresponding pyridinium-ionic liquids with halide. Eftakhari and Saito^[31] once concluded that larger counter anions lower the Tg due to their bulkiness and distributed charges. As shown in Figs. 2 and 3, and Table 1, pyridinium ionic liquids with hexafluorophosphate counter anion exhibit high melting temperature than their halide counterparts in this study. These results are agreement with the results

obtained from the thermogravimetric analyses, which suggested that pyridinium ILs with hydrophobic counter anion are more stable than those with halide counter anion counterpart.



Figure 2 DSC overlay thermograms of pyridinium ionic liquids with halide

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Figure 3 DSC thermograms of pyridinium ionic liquids with PF_6^- , [N-propylPyr]⁺[PF₆]⁻ (A), and [N-isopropylPyr]⁺[PF₆]⁻ (B).

3.3.3 Conductivity

The conductivity measurements of pyridinium ionic liquids with halide anion were obtained in aqueous solution (water), while those of hydrophobic pyridinium ionic liquids with hexafluorophosphate anioin were obtained in DMSO. Table 1 show conducitivities obtained for the synthesized ionic liquids and temperatures at which the measurements were recorded. It is

evident that pyridinium ILs with halide have higher conductivities compared to those with hexafluorophosphate anion. In terms of isomeric alkyl chain length at the N-position of pyridinium cation, pyridinium ionic liquids with propyl group were found to have higher conductivities than those with isopropyl group. Dharaskar *et al.* ^[30] once reported a small ionic conductivity of 1-butyl-3-methylimidazolium tatrafluoroborate and they concluded that the ionic liquid conductivity is mainly influenced by the mobility of its own cation because of the diffusion coefficients differences between the cation (higher) and anion (lower). Therefore, it can be concluded that an increase in alkyl chain length also increases the conductivity of that particular ionic liquid.

Table 1 Melting point (T_m) , glass transition (T_g) , decomposition (T_d) temperatures in degrees Celsius, and ionic conductivity (σ , mS) at given temperatures.

Ionic Liquid	T _m (°C)	T _g (°C)	T _d (°C)	σ(mS)	
[N-propylPyr][Br]	67	28	291	241 at 22°C	
[N-IsopropylPyr][Br]	59	25	293	1.197 at 22°C	
[N-propylPyr][PF6]	92	26	289	0.643 at 24°C	
[N-isopropylPyr][PF ₆]	89	24	543	0.334 at 24°C	

N-ProyIPyr*][Br-] isopropy/Pyr.)[Br

3.3.4 Solubility of synthesized ionic liquids

Figure 4 Solubility studies of the synthesized ILs in a range of aqueous and organic solvents. Polar protic: water (H₂O) and methanol (MeOH), Non-polar: hexane (HEX) and chloroform (CHCl₃), and Polar aprotic: dimethyl sulfoxide (DMSO) and dimethy formamide (DMF). Soluble (S) and Non-soluble (N.S).

The solubility of the syntthesized ILs was determined by dissolving equal amount of ILs in different aqueous and organic solvents. Owing to the type of counter anion, and/or isomeric carbon lateral chain involved, these ILs showed variable solubility characteristics as shown in Fig. 4. It has been established that a solvent or solute will only dissolve or be dissolved in a substance of

similar polarity, respectively ("like dissolves likes"). However, as shown in Fig. 4 (A), [NpropylPyr]⁺[Br]⁻ was soluble in polar protic and non-polar solvents, and slightly insoluble in polar aprotic solvents. This behaviour can be correctly linked to the formation of hydrogen bonding (intermolecular forces) between the polar protic or non-polar solvents and ILs. On the other hand, $[N-Isopropy|Pyr]^+[Br]^-$ behaved comparable different and showed significant miscibility only in non-polar solvents. The hydrophilic character and the formation of hydrogen bonding are responsible for this latter-IL behaviour in aqueous and organic medium. Another thing worthy to be mentioned which comparable affect the solubility of ILs is the alkyl lateral chain. It is evident that pyridinium-ILs with straight-lateral alkyl chain attached on pyridinium-nitrogen atom are more soluble in aqueous and organic medium than their corresponding isomeric counterparts. Hydrophobic [N-propylPyr]⁺[PF₆]⁻ and [N-isopropylPyr]⁺[PF₆]⁻ ionic liquids were observed to be insoluble in all polar protic and non-polar solvents, yet soluble in DMSO. The hydrophobicity of these ILs and large dielectric constant of DMSO played significantly role in the insolubility of the ILs in other solvents except DMSO.

Ionic liquids	Polar protic		Non-polar		Polar aprotic	
	H ₂ O	МеОН	HEX	CHCl ₃	DMSO	DMF
[N-propylPyr][Br]	S	S	S	N.S	N.S	N.S
[N-IsopropylPyr][Br]	Slightly S	Slightly S	N.S	N.S	S	S
[N-propylPyr][PF ₆]	Slightly Suspended	N.S	N.S	N.S	Slightly S	Slightly S
[N-isopropylPyr][PF ₆]	N.S	N.S	N.S	N.S	S	S

Table 2 Solubility tests of ionic liquids in different solvents. Some are soluble (S), slightly soluble, or non-soluble (N.S) in polar protic, non-polar or polar aprotic solvents.

The results obtained for [*N*-propylPyr]⁺[PF₆]⁻ and [*N*-isopropylPyr]⁺[PF₆]⁻ from liquid chromatography showed that the ionic liquids could not be identified and there were no retentions times recorded for these ionic liquids. It was observed that these two ionic liquids could not go through the SPE packing because they were insoluble in methanol and water. The absence of these ionic liquids from the solution collected by SPE tank is a direct indication that these ionic liquids are immiscible in both methanol/water used for SPE, and also mobile phase used in the Liquid chromatography.

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4. Conclusions

Four ionic liquids were successfully synthesized and their purity was confrimed by NMR and FTIR spectroscopic studies. Pyridinium based ionic liquids with halide counter anion were observed to be stable below 400 °C and were less stable than their hexafluorophosphate counterparts. Carbon loss was identified at temperatures above 700 °C. In terms of the alkyl chain isomerism, pyridinium-ionic liquids with isopropyl alkyl group on N-position of pyridinium cation were significantly more stable than ionic liquids with propyl group. However, pyridinium-ionic liquids with propyl alkyl group were found to have high conductivity than isopropyl containing ionic liquids. Studies on solubilities of these ionic liquids showed that hexafluorphosphate containing ionic liquids were insoluble in water (hydrophobic).

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Supporting information (SI): FT-IR spectra of four as-synthesized ionic liquids (SI. 01), all NMR spectra of ionic liquids studied in this current work (SI. 02-05) and accurate mass analysis (SI.06-07).

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