Journal of Molecular Liquids 221 (2016) 1140–1144

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Nitrile-functionalized azepanium ionic liquids: Synthesis characterization and thermophysical properties

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ARTICLE INFO

Article history:
Received 19 October 2015
Received in revised form 23 May 2016
Accepted 27 June 2016
Available online 01 July 2016

Keywords:
Azepane
Nitrile functionality
Biomass dissolution
Ionic liquids
Thermal stability
Melting point

ABSTRACT

The synthesis of nitrile-functionalized azepanium ionic liquids such as 1-butyl-1-(2-cyano-ethyl)-azepanium bromide, [C_{4CN}Azp][Br], 1-butyl-1-(2-cyano-ethyl)azepanium trifluoroacetate, [C_{4CN}Azp][TFA], 1-butyl-1-(2-cyano-ethyl)-azepanium methanesulfonate [C_{4CN}Azp][CH_3SO_3], 1-butyl-1-(2-cyano-ethyl)azepanium trifluoromethanesulfonate [C_{4CN}Azp][CF_3SO_3], 1-butyl-1-(2-cyano-ethyl)azepaniummethanesulfate[C_{4CN}Azp][CH_3SO_4],1-butyl-1-(2-cyano-ethyl) azepanium *p*-toluenesulfonate [C_{4CN}Azp][PTS] were performed. The synthesis of ionic liquids was performed in three steps. ^{1}H, ^{13}C and CHNS elemental analysis were used to characterize the synthesized ionic liquids. The thermal stability, melting point and glass transition temperature of the ionic liquids were determined. The nitrile-functionalized ionic liquids showed good thermal stability.

1. Introduction

Ionic liquids (ILs) are organic salt consisting entirely of ions [1]. If they are liquids at ambient conditions, they can be termed as room temperature ionic liquids (RTILs). Most of the ILs are synthesized from five and six membered aromatic or non-aromatic cyclic compounds containing a nitrogen atom [2–4] For instance, the most extensively studied ILs are based on 1-alkyl-3-methylimidazolium cation. Although ILs with bicyclic ring systems was reported [5,6], there is only limited number of ILs with seven membered heterocyclic systems [5,7–9]. The properties of ILs can be adjusted by the careful section of the constituent ions. Because of this properties ILs find applications in different areas such as separation [10–14], electrochemistry [15], biomass dissolution [16–19], and organic synthesis [20,21]. The properties can be enhanced by the incorporation of functional groups. The class of ILs with functional groups is known as functionalized ionic liquids. The functional groups can be introduced either to cation or to anion or on both. In 1998, Davis et al. reported the synthesis first functionalized ILs from miconazole [22]. After this report, many functionalized ILs were synthesized for various applications [2,23–26]. Among the functionalized ILs nitrile-functionalized ILs have special place because of their higher thermal stability [27]. The nitrile-functionalized ILs with five and six ring systems (imidazolium, pyrrolidinium, pyridinium and pypiridinium) were investigated for various applications [27–30]. However, there is no report regarding nitrile-functionalized ILs with seven membered ring (azepane) systems. The azepanium based ILs were first introduced by Belhocine et al. [7,9]. They reported the thermophysical properties of azepanium ILs having side chains such as butyl, hexyl, methoxyethyl and 1-ethoxy-2-methoxy-ethane with various anions such as bistriflimide, trifluoroacetate and trifluoromethanesulfonate. Azepanium based ILs also been reported for other applications such as electrolyte for high voltage super capacitors, and electro chemistry [8,9,31–33]. In this work, the synthesis and characterization of nitrile-functionalized azepanium ILs with various anions such as trifluoro acetate, methanesulfonate, and methane sulfate were reported. These ILs were developed in order to explore their potential in biomass dissolution. The biomass dissolution experiments are currently in progress in our laboratory. Preliminary results showed that nitrile functionalized ILs, especially triflate and trifluoro acetate anion containing ILs, are promising solvents for the dissolution of biomass.

2. Experimental

The starting materials and reagents were purchased from Acros Organics. All the starting materials were used without further purification.

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http://dx.doi.org/10.1016/j.molliq.2016.06.092
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An elemental analyzer (EA-1110) was used to measure carbon, hydrogen and nitrogen content of the ionic liquids. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer. The thermal decomposition temperature was measured using a thermal gravimetric analyzer (Perkin-Elmer, Pyris V-3.81). The samples were heated in an inert atmosphere from 50 °C to 750 °C at a heating rate of 10 °C min^{-1}. The uncertainty of the measurement is ± 1 °C. Melting point and glass transition temperature was measured using differential scanning calorimetry (DSC; PerkinElmer, model Pyris1).

2.1. Synthesis of 3-Azepan-1-yl-propionitrile

To a solution of Azepane (2 g, 20.16 mmol), acrylonitrile was added and stirred at room temperature for 24 h. The reaction mixture was poured into water and the organic layer was extracted with dichloromethane (3 × 10 mL). The combined organic layer was evaporated using a rotary evaporator to obtain 3-Azepan-1-yl-propionitrile as a pale yellow liquid. Yield = 2.7 g (88%). ^{1}H NMR (DMSO,d$_6$): δ: 1.21 (m, 4H), 1.40 (m, 4H), 2.41 (m, 4H), 2.55 (t, 2H), 2.80 (t, 2H). ^{13}C NMR, DMSO (d$_6$): δ: 17.2, 26.4, 29.6, 49.4, 117.2. CHN elemental analysis: Calculated: C; 71.01, H; 10.59, N; 18.40. Experimental: C; 69.98, H; 10.66, N; 18.34.

2.2. Synthesis of 1-butyl-1-(2-cyano-ethyl)-azepanium bromide [C$_{4CN}$Azp][Br]

To a solution of 3-Azepan-1-yl-propionitrile (3 g, 19.70 mmol) in acetonitrile (15 mL), 1-bromobutane (3.24 g, 23.64 mmol) was added and stirred at 55 °C for 48 h. The acetonitrile was evaporated using a rotary evaporator and the solid obtained was washed with ethyl acetate (3 × 15 mL). The residual solvent was removed using rotary evaporator and the product was further dried in vacuum oven at 50 °C for 24 h. Yield = 3.5 g (61%). ^{1}H NMR (DMSO, d$_6$): $\delta = 0.90$ (t, 3H), 1.35 (m, 2H), 1.78 (m, 6H), 1.22(m, 4H), 3.10(m, 6H), 3.28 (m, 2H), 3.58 (m, 2H). ^{13}C NMR (DMSO, d$_6$): 12.8, 19.2, 21.1, 24.2, 26.2, 28. 5, 56.2, 60. 9, 63.2, 117.2. CHN elemental analysis: Calculated: C; 53.98, H; 8.71, N; 9.68. Experimental: C; 54.14, H; 8.89, N; 9.61.

2.3. 1-Butyl-1-(2-cyano-ethyl)azepanium trifluoroacetate [C$_{4CN}$Azp][TFA]

To a solution of [C$_{4CN}$Azp][Br] (5 g, 17.27 mmol) in dichloromethane (25 mL), sodium trifluoroacetate (2.58 g, 19.0 mmol) was added and stirred at room temperature for 24 h. The precipitate formed was filtered off and the organic phase was washed several times with ice cold water. The dichloromethane was removed using rotary evaporator and the product obtained was further dried in vacuum oven at 50 °C for 24 h. The [C$_{4CN}$Azp][TFA] obtained as a pale yellow solid. Yield = 5 g (89%). ^{1}H NMR (DMSO, d$_6$): $\delta = 0.90$ (t, 3H), 1.35 (m, 2H), 1.78 (m, 6H), 1.22 (m, 4H), , 3.10 (m, 6H), 3.28 (m, 2H), 3.58 (m, 2H). ^{13}C NMR (DMSO, d$_6$): 12.4, 19.6, 21.9, 23.2, 26.4, 28. 1, 56.0, 60. 1, 62.3, 117.7. 128.3(q), 178.6. CHN elemental analysis: Calculated: C; 55.89, H; 7.82, N; 8.69. Experimental: C; 55.84, H; 7.89, N; 8.78.

2.4. 1-Butyl-1-(2-cyano-ethyl)-azepanium methanesulfonate [C$_{4CN}$Azp][CH$_3$SO$_3$]

[C$_{4CN}$Azp][CH$_3$SO$_3$] was synthesized by the same procedure described for [C$_{4CN}$Azp][TFA] using [C$_{4CN}$Azp][Br] (10 g, 34.57 mmol) and sodiummethanesulfonate (4.49 g, 38.02 mmol). Yield = 8 g (76%).^{1}H NMR (DMSO, d$_6$): $\delta =$) δ =0.90 (t, 3H), 1.35 (m, 2H), 1.78 (m, 6H), 1.22 (m, 4H), 3.10 (m, 6H), 3.28 (m, 2H), 3.58 (m, 2H), 3.91 (s, 3H). ^{13}C NMR (DMSO, d$_6$): 12.1, 19.5, 21.8, 23.2, 26.4, 28. 3, 58.10, 56.0, 60. 1, 62.3, 117.7. CHN elemental analysis: Calculated: C; 55.23, H; 9.27, N; 9.20. Experimental: C; 55.29, H; 9.21, N; 9.15.

2.5. 1-Butyl-1-(2-cyano-ethyl)azepanium trifluoromethanesulfonate [C$_{4CN}$Azp][OTf]

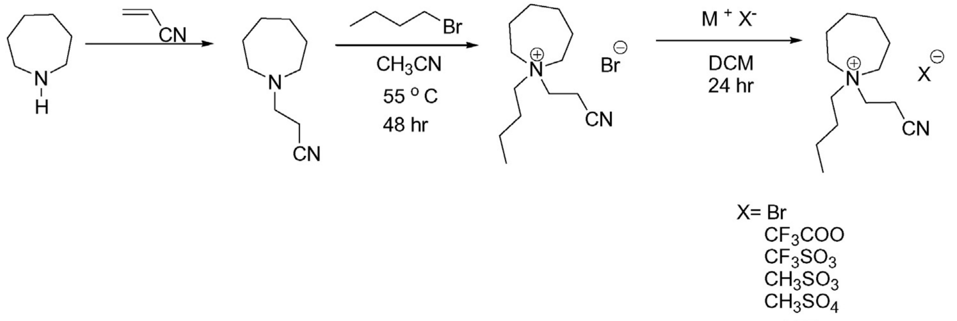
[C$_{4CN}$Azp][CF$_3$SO$_3$] was synthesized by the same procedure described for [C$_{4CN}$Azp][TFA] using [C$_{4CN}$Azp][Br] (6 g, 20.74 mmol) and potassium trifluoro methanesulfonate (4.29 g, 22.81 mmol). Yield = 5 g (67%).^{1}H NMR (DMSO, d$_6$):$\delta =_N$: 0.90 (t, 3H), 1.35 (m, 2H), 1.78 (m, 6H), 1.22 (m, 4H), , 3.10 (m, 6H), 3.28 (m, 2H), 3.58 (m, 2H). ^{13}C NMR (DMSO, d$_6$): 12.4, 19.6, 21.9, 23.2, 26.4, 28. 1, 56.0, 60. 1, 62.3, 117.7. 125.3(q). CHN elemental analysis: Calculated: C; 46.91, H; 7.03, N; 7.82. Experimental: C; 46.85, H; 7.09, N; 7.86.

2.6. 1-Butyl-1-(2-cyano-ethyl)azepanium methanesulfonate [C$_{4CN}$Azp][CH$_3$SO$_4$]

[C$_{4CN}$Azp][CH$_3$SO$_4$] was synthesized by the same procedure described for [C$_{4CN}$Azp][TFA] using [C$_{4CN}$Azp][Br] (6 g, 20.74 mmol) and sodiummethanesulfonate (3.05 g, 22.81 mmol). Yield = 5.2 g (66%).^{1}H NMR (DMSO, d$_6$):$\delta = \ =$ 0.90 (t, 3H), 1.35 (m, 2H), 1.78 (m, 6H), 1.22(m, 4H), 3.10(m, 6H), 3.28 (m, 2H), 3.58 (m, 2H)., 3.81(s, 3H). ^{13}C NMR (DMSO, d$_6$): 12.1, 19.5, 21.8, 23.2, 26.4, 28. 3, 56.10, 56.0, 60. 1, 62.3, 117.7. CHN elemental analysis: Calculated: C; 52.47, H; 8.81, N; 8.74. Experimental: C; 52.39, H; 8.91, N; 8.68.

2.7. 1-Butyl-1-(2-cyano-ethyl)azepanium p-toluenesulfonate [C$_{4CN}$Azp][PTS]

^{1}H NMR (DMSO, d$_6$): $\delta = 0.90$ (t, 3H), 1.35 (m, 2H), 1.78 (m, 6H), 1.22 (m, 4H), 2.35 (s, 3H), 3.10 (m, 6H), 3.28 (m, 2H), 3.58 (m, 2H), 7.31 (d, 2H), 7.89 (d, 2H). ^{13}C NMR (DMSO, d$_6$): 12.8, 19.2, 20.8, 21.1, 24.2, 26.2, 28. 5, 56.2, 60. 9, 63.2, 117.2, 125.4, 130.8, 135.9. CHN elemental analysis: Calculated: C; 63.60, H; 9.15, N; 7.06. Experimental: C; 63.51, H; 9.11, N; 7.15.



Scheme 1. Synthesis route for nitrile-functionalized azepanium ILs.

Table 1
Thermal decomposition temperature (T_d), melting point (T_m) and glass transition temperature (T_g) of the ILs.

ILs	T_d (°C)	Tm (°C)	T_g (°C)
[C_{4CN}Azp][Br]	216	164	nd
[C_{4CN}Azp][TFA]	176	80	−60
[C_{4CN}Azp][CH_3SO_3]	220	142.9	−10
[C_{4CN}Azp][OTf]	332	104.6	−82
[C_{4CN}Azp][CH_3SO_4]	234	168.4	−20
[C_{4CN}Azp][PTS]	240	158.6	nd

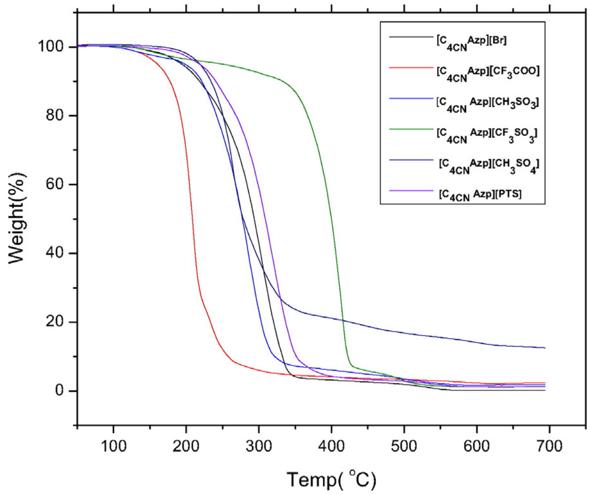


Fig. 2. TGA profile of the synthesized ILs: [C_{4CN}Azp][OTf], [C_{4CN}Azp][PTS], [C_{4CN}Azp][CH_3SO_4], [C_{4CN}Azp][CH_3SO_3], [C_{4CN}Azp][Br], [C_{4CN}Azp][TFA].

3. 2. Results and discussion

The synthesis of nitrile-functionalized ILs was performed in three steps according to the Scheme 1.

In the first step, nitrile-functionality was introduced by the reaction of azepane with acrylonitrile at room temperature in solvent free condition. The reaction mixture was poured into to water and the product was extracted using dichloromethane. The solvent was removed using rotary evaporator and Azepanepropionitrile was obtained as a pale yellow liquid in excellent yield (98%). In the second step, the bromide salt was synthesized by the reaction of 3-Azepan-1-yl-propionitrile with 1-bromobutane at 55 °C for 48 h. Acetonitrile was used as the solvent. After the removal of the solvent and washing with ethyl acetate, [C_4CNAzp][Br] was obtained as a white solid. The third step was the introduction of various anions by the ion exchange reaction of the bromide precursor ILs with the metal salts of the desired anions. The reaction was performed at room temperature in dichloromethane for 24 h. The precipitate formed was filtered off and the solution was washed with several times with aliquot of cold water to remove the remaining halide impurities. The halide content was measured using ion chromatogram and was found to be below 250 ppm. The nitrile-functionalized azepanium ILs obtained as solids at room temperature. The structure, name and abbreviations of the synthesized ILs is given in Table 1.

The synthesized ILs were mainly characterized using ^{1}H NMR. ^{1}H NMR spectrum of [C_{4CN}Azp][Br] is shown in Fig. 1.

A triplet at $\delta = 0.90$ corresponds to the three protons on methyl (–CH_3) group at the end of the carbon in the alkyl chain (marked a in the structure). The multiplets at $\delta = 1.35$, corresponds to the **b**. The multiplet at around $\delta = 1.3$ corresponds to **i** and **c**. The multiplets at $\delta = 1.78$ represents the hydrogen atoms **h**. Another multiplet at $\delta = 3.1$ corresponds to **g** and **f**. The multiplets at around $\delta = 3.2$ and $\delta = 3.4$ represents **e** and **d** respectively. The peak at 2.5 corresponds to the solvent residual peak (DMSO) and another singlet at 3.33 corresponds to the water in the DMSO.

The thermal stability of the synthesized ILs were determined using thermo gravimetric analysis (TGA) and the results are given in Table 1 and Fig. 2.

Among all the ILs studied, [C_{4CN}Azp][OTf] showed the highest thermal stability (332 °C). The azepanium ILs with simple alky groups also showed similar thermal behavior [7]. For instance, the methylazepanium cation with butyl group with [OTf] anion (1-butyl-1-methyl azepanium triflate, [C_4mAzp][OTf]) is thermally stable up to 310 °C, which is only about 20 °C lower than [C_{4CN}Azp][OTf]. Similar results were obtained when the alkyl group on the azepanium ring was changed to hexyl group. 1-Hexyl-1-methyl azepanium triflate, [C_6mAzp][OTf] is also stable up to 310 °C. [C_{4CN}Azp][TFA] showed a thermal stability of 176 °C, which is comparable to the thermal stability of azepanium ILs with simple alkyl side chain having the similar anion [34]. For instance, the thermal stability of 1-butyl-1-methyl azepanium trifluoroacetate, [C_4Azp][TFA] is 170 °C. Similar results were observed in the case of azepanium cation with hexyl group, [C_6Azp][TFA], which is also stable up to 170 °C. Azepanium based protic ILs with trifluoroacetate anion, [Azp][TFA] is thermally more stable (239 °C) than [C_6Azp][TFA] and [C_{4CN}Azp][TFA] [8]. The thermal stability of the synthesized ILs follows the order

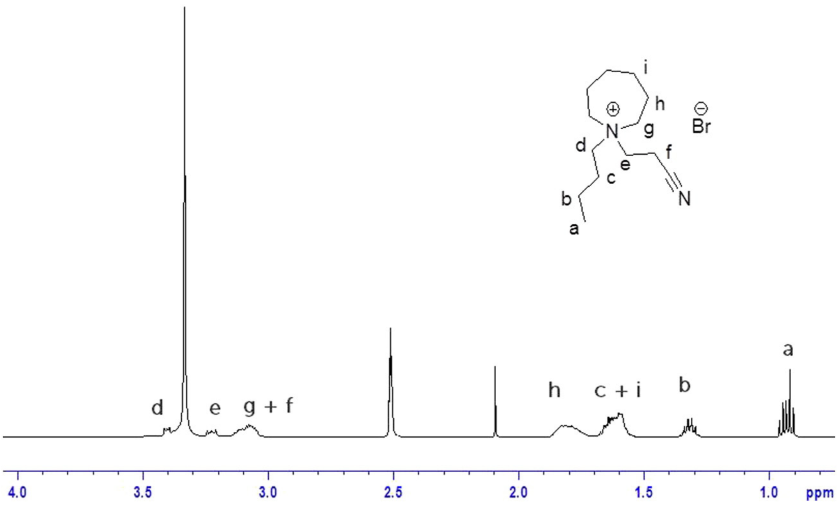


Fig. 1. ^{1}H NMR spectrum of [C_{4CN}Azp][Br].

[C$_{4CN}$Azp][OTf] > [C$_{4CN}$Azp][PTS] > [C$_{4CN}$Azp][CH_3SO_4] > [C$_{4CN}$Azp][CH_3S-$_3SO_3$] > [C$_{4CN}$Azp][Br] > [C$_{4CN}$Azp][TFA]. The bromide salt showed 5% decomposition at 192 °C. Most thermally stable [C$_{4CN}$Azp][OTf] among the studied ILs showed less than 2% decomposition at similar temperature. About 20% of mass loss was observed in the case of [C$_{4CN}$Azp][TFA], while [C$_{4CN}$Azp][PTS] decomposed only around 2% at the similar experimental conditions. The melting point and glass transition of the studied ILs were determined using DSC and the results are tabulated in Table 2. As expected, the bromide salt showed the highest melting point among the studied ILs. The higher melting points of the bromide salt attributed to the stronger interaction between the cation and the bromide anion. The lowest melting point was observed for [C$_{4CN}$Azp][TFA](80 °C). The melting points of the synthesized ILs follow the order [C$_{4CN}$Azp][Br]>[C$_{4CN}$Azp][CH_3SO_4]>[C$_{4CN}$Azp][PTS]>[C$_{4CN}$Azp][CH_3SO_3] > [C$_{4CN}$Azp][OTf] > [C$_{4CN}$Azp][TFA]. Melting point of azepanium ILs with nitrile-functionality is higher than azepanium ILs with simple alkyl groups. For instance, the melting point of [C$_6$mAzp][OTf] and [C$_4$mAzp][OTf] is 98 °C and 55 °C respectively, which is lower than the melting point of [C$_4$CNAzp][OTf] (104 °C). Similar result was observed in the case of [C4CNAzp][TFA]. Melting point of [C4CNAzp][TFA] is about 35 °C higher than [C6mAzp][TFA] and about 10 °C higher than [C4mAzp][TFA]. The higher melting point of the nitrile-functionalized ILs attributed to the increased H-bonding interaction [35] caused by the incorporation of nitrile functionality due to the partial negative charge on the nitrile group [2]. All the nitrile-functionalized ILs showed glass transition temperature except [C$_{4CN}$Azp][Br] and [C$_{4CN}$Azp][PTS]. ILs with anion containing fluorine atom showed lowest glass transition temperature. For instance, [C$_{4CN}$Azp][OTf] showed the lowest glass transition temperature(−82 °C). On the other hand ILs without the fluorine atom, [C$_{4CN}$Azp][CH_3SO_3] showed the highest T_g (−10 °C). This lower T_g associated with the fluorine containing anions attributed to the lower van der Waals interaction between the cation and anion [36]. The azepanium based ILs without the nitrile-functionality showed a different thermal behavior compared to the nitrile-functionalized ones. For example [C$_4$mazp][TFA] showed no glass transition. However, the T_g of nitrile-functionalized analogue, [C$_{4CN}$Azp][TFA] is −60 °C [34].

4. Conclusion

Nitrile-functionalized azepanium ILs with different anions were synthesized and characterized. ^{1}H NMR, ^{13}C NMR and CHN elemental analysis were used to characterize ILs. The melting point, glass transition and thermal decomposition temperature of the ILs were determined using thermo gravimetric analysis (TGA) and Differential scanning calorimetry (DSC). All the ILs showed good thermal stability. 1-butyl-1-(2-cyano-ethyl)azepanium trifluoromethanesulfonate, [C$_{4CN}$Azp][OTf], showed the highest thermal stability among the synthesized ILs. [C$_{4CN}$Azp][Br] has the highest melting point among the studied ILs.

Acknowledgement

This work was supported by Short Term Internal Research Grant (STIRF, cost center: 0153AA-C31) from Universiti Teknologi PETRONAS (UTP).

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