Influence of ion structure on thermal runaway behaviour of aprotic and protic ionic liquids

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Electronic Supporting Information

Experimental Details

Ionic Liquids

1-methylimidazole (99%), bis(fluorosulfonyl)imide (99%), Tetrabutylphosphonium hydroxide (40 wt. % in water), 1-methyl-propyl-pyrrolidinium methyl carbonate (50 wt. % in water), Tetramethylammonium hydroxide (25 wt. % in water), N, N − diethylmethylamine (99.5%) and Triflic acid (98%) were purchased from Sigma and used without any further purification. The general synthesis of protic ionic liquids involve the proton transfer from the corresponding acid to the corresponding base *while* the aprotic ionic liquids were made either by the reaction of the corresponding cation hydroxide with the acids (eliminating water) or by the reaction of cation methyl carbonate with the acids (eliminating water and methanol). In the case of protic ionic liquids, the acid base stoichiometry was confirmed by determining the pH of a 0.1 M aqueous solution of the material. This was found to be in satisfactory agreement with a control aqueous sample. After the synthesis, the protic and aprotic ionic liquids were dried under vacuum (0.1Pa, room temperature) for 8 h. The water content present in the protic and aprotic ionic liquids were in the range of 500-600ppm and 180-190ppm respectively. It was not possible to load the samples into the ARC bomb calorimeter

under completely dry conditions, however the process was carried out as quickly as possible (1-2 mins). The individual synthesis and characterization of protic and aprotic ionic liquids are described in detail below:

1.0 Synthesis of Protic ionic liquids:

1.1 Synthesis of 1-methyl-3H-imidazolium bis(fluorosulfonyl)imide [Hmim][FSI]

1-methyl imidazole (2 g, 0.024 moles) and bis(fluorosulfonyl)imide (4.4 g, 0.024 moles) were mixed in distilled water (50 mL) at 0 ˚C for 2h. The solution was concentrated *in vacuo* to give an off-white solid (6.3 g, yield 98.4%). 1H NMR (d-DMSO): δ 10.9 ppm, 1H, s (broad) ; δ 8.8 ppm, 1H, s ; δ 7.8, 1H, d ; δ 7.5, 1H, d, t ; δ 3.50 ppm, 3H, s ; 13C NMR : δ 130.2 ppm, ; δ 120.1 ppm ; δ115.6 ppm ; δ 35.1 ppm. MS [ES]$^+$ = 83.2 ; MS [ES]$^-$ = 179.7.

1.2 Synthesis of N, N-diethylmethylammonium bis(fluorosulfonyl)imide [HN$_{122}$][FSI]

N, N - diethylmethylamine (2.41 g, 0.057 moles) and bis(fluorosulfonyl)imide (5.0 g, 0.023 moles) were mixed in distilled water (50 mL) at room temperature for 3h. The solution was concentrated in vacuo to give a clear oil (4.95 g, yield 99 %). 1H NMR (d-DMSO): δ7.3 ppm, 1H, s (broad) ; δ 3.3 ppm, 4H, q ; δ 3.0, 3H, s ; δ 1.8, 6H, t ; 13C NMR : δ 50.1 ppm, ; δ 45 ppm ; δ 10 ppm. MS [ES]$^+$ = 88.1; MS [ES]$^-$ = 179.9.

1.3 Synthesis of 1-methyl-3H-imidazolium triflate [Hmim][Tf]

Aqueous solution of triflic acid (6.5g, 0.043moles) was slowly added to aqueous 1-methyl imidazole (3.5 g, 0.043 moles) in an ice bath and the contents were stirred for 1h. Then water was concentrated *in vacuo* to give white solid (9.84 g, yield 98.4%). MS [ES]$^+$ =83.1 ; MS [ES]$^-$ = 149.3. Melting point = 112 ºC. ^{1}H NMR (400.20 MHz in D$_2$O, δ, ppm relative to TMS): 3.8(s, 3H), 7.4(m, 2H), 8.5(s, 1H). ^{13}C NMR: δ 35.4 ppm, ; δ 38.5 ppm ; δ 114.5 ppm ; δ 119.5 ppm ; δ 124.4 ppm ; δ 134.9 ppm.

1.4 Synthesis of N, N-diethylmethylammonium triflate [HN$_{122}$][Tf]

Aqueous solution of triflic acid (6.3g, 0.042moles) was slowly added to aqueous N, N - diethylmethylamine (3.7g, 0.042moles) in an ice bath and the contents were stirred for 1h. Then water was concentrated *in vacuo* to give white solid (9.85g, yield 98.5%). ^{1}H NMR (400.20 MHz in CDCl$_3$, δ, ppm relative to TMS): 1.37(s, 6H), 2.80(s, 3H), 3.1-3.3(m, 4H), 8.1(s, 1H) ; MS [ES]$^+$ = 88.1 ; MS [ES]$^-$ = 149.1.

1.5 Synthesis of 1-methyl-3H-imidazolium methanesulfonate [Hmim][MS]

Aqueous solution of methanesulfonic acid (5.4g, 0.056moles) was slowly added to aqueous 1-methyl imidazole (4.6g, 0.056moles) in an ice bath and the contents were stirred for 1h. Then water was concentrated *in vacuo* to give white solid (9.8g, yield 98.0%). MS [ES]$^+$ = 83.1 ; MS [ES]$^-$ = 95.1; Melting point = 130 ºC. ^{1}H NMR (400.20 MHz in D$_2$O, δ, ppm relative to TMS): 2.7(s, 3H), 3.8(s, 3H), 7.4(m, 2H), 8.6(s, 1H). ^{13}C NMR: δ 35.5 ppm, ; δ 38.5 ppm ; δ 119.5 ppm ; δ 123.0 ppm ; δ 135.0 ppm.

2.0 Synthesis of Aprotic ionic liquids:

2.1 Synthesis of tetrabutylphosphonium bis(fluorosulfonyl)imide [P$_{4444}$][FSI]

Tetrabutylphosphonium hydroxide (40 wt. % in water) (7.86 g, 0.011 moles) and bis(fluorosulfonyl)imide (2.06 g, 0.011 moles) were mixed in distilled water (50 mL) at room temperature for 3h. The solution was concentrated *in vacuo* to give a clear oil (4.95 g, yield 99 %). 1H NMR (d-DMSO): δ 2.50 ppm, 8H, t ; δ 1.55 ppm, 8H, m ; δ 1.38, 8H, m ; δ 0.9, 12H, t ; 13C NMR : δ 30.2 ppm, ; δ 26.7 ppm ; δ 20.1 ppm ; δ 15.0 ppm. MS [ES]$^+$ = 258.9 ; MS [ES]$^-$ = 179.9.

2.2 Synthesis of 1-methyl-propyl-pyrrolidinium bis(fluorosulfonyl)imide [C₃mpyr][FSI]

1-methyl-propyl-pyrrolidinium methyl carbonate (50 wt. % in water) (6.6 g, 0.016 moles) and bis(fluorosulfonyl)imide (2.94 g, 0.016 moles) were mixed in distilled water (50 mL) at room temperature for 3h. The solution was concentrated *in vacuo* to give a clear oil (4.98 g, yield 99.6 %). 1H NMR (d-DMSO): δ 3.35 ppm, 3H, s ; δ 3.25 ppm, 2H, t ; δ 3.22, 4H, t ; δ 1.9, 2H, m, t ; δ 1.7 ppm, 4H, t ; δ 0.92 ppm, 3H, t ; 13C NMR : δ 65.5 ppm, ; δ 50.1 ppm ; δ 24.3 ppm ; δ 17.1 ppm ; δ 12.3 ppm. MS [ES]$^+$ = 127.9 ; MS [ES]$^-$ = 179.9.

2.3 Synthesis of tetramethylammonium bis(fluorosulfonyl)imide [N₁₁₁₁][FSI]

Tetramethylammonium hydroxide (25 wt. % in water) (7.16 g, 0.012 moles) and bis(fluorosulfonyl)imide (3.55 g, 0.019 moles) were mixed in distilled water (50 mL) at room temperature for 3h. The solution was concentrated *in vacuo* to give a white solid (4.95 g, yield 99 %). 1H NMR (d-DMSO): δ 3.50 ppm, 12H, s ; 13C NMR : δ 60 ppm. MS [ES]$^+$ = 74.1 ; MS [ES]$^-$ = 179.9 ; Melting point = 77 ºC.

3.0 DFT methodology

The orbitals were generated as virtual orbitals from a wB97XD DFT[34, 35] calculation in Gaussian[16, 34-36].
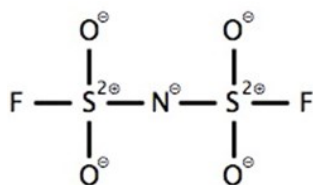
Scheme 1: The schematic representation of FSI anion.

3.0 ARC Experimentation

The thermal run away and intrinsic safety of different protic and aprotic ionic liquids were investigated by Accelerated Rate Calorimeter (ARC) technique. The instrument works on a "heat-wait-measure" principle and has been widely employed to investigate thermal runaway of exothermic systems[1]. The ARC records self- heat rate as a function of temperature and also gives time vs temperature and pressure vs temperature profiles. In order to compare the self-heat rates, the experiments were carried out with identical sample weights (in order to achieve similar thermal inertiaΦ). The ionic liquid samples (typically 0.5 to 1g) were loaded in the ARC sample bomb (made of titanium), connected with thermocouples and pressure transducer and enclosed in a shielded environment as given in figure below. The samples were then subjected to heat-wait-search mode and the outputs were recorded and analyzed.
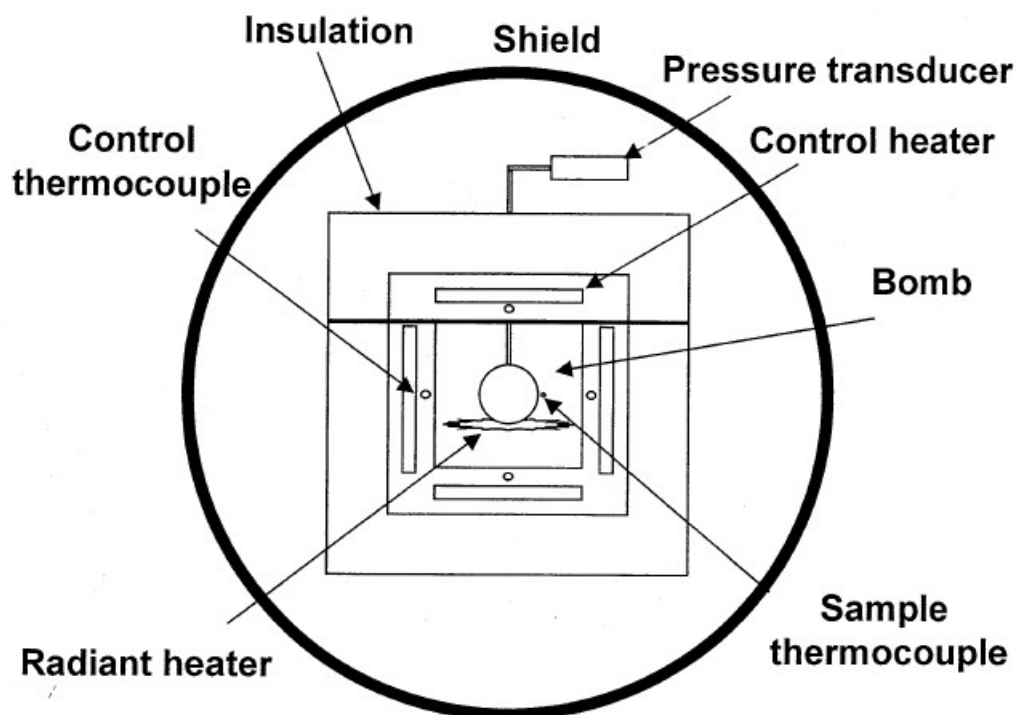
Accelerating rate calorimeter (Fig adopted from Current science, Vol. 80, page 744, 2001)

The thermal inertia (ϕ), correction refers to the compensation of heat loss to the sample container during the test, which is computed using the following formula (ASTM E1981):

$$\phi = \frac{(m_s C_{p,s} + m_c C_{p,c})}{m_s C_{p,s}}$$

$$\phi = 1 + \frac{m_c C_{p,c}}{m_s C_{p,s}}$$

m_c = mass of the container

m_s = mass of the sample

$C_{p,c}$ = heat capacity of the container

$C_{p,s}$ = heat capacity of the sample

This correction is important in ARC studies as the mass of the sample is quite small in comparison to the mass of the container, therefore there is a loss of heat energy to the container, whereas industrial scale reactors, there is no such loss (ϕ always remains as 1).

Table S1: Summary of accelerated rate calorimeter date for various ionic liquids

| Ionic liquid	T_{onset} (°C)	T_{final} (°C)	ΔT_{ad} (°C)	ΔT_{ab} (°C)	ΔH (J/g) ±5%
[Hmim] [FSI]	341	353	13	33	72
[P$_{4444}$] [FSI]	196	328	132	353	764
[C$_3$mpyr] [FSI]	199	326	153	404	887
[N$_{111}$] [FSI]	248	378	130	650	531
[HN$_{122}$] [FSI]	175	367	191	501	1073
[Hmim] [Tf]	352	451	99	701	401
[HN$_{122}$] [Tf]	236	450	213	559	1181
[Hmim] [MS]	330	353	22	58	124
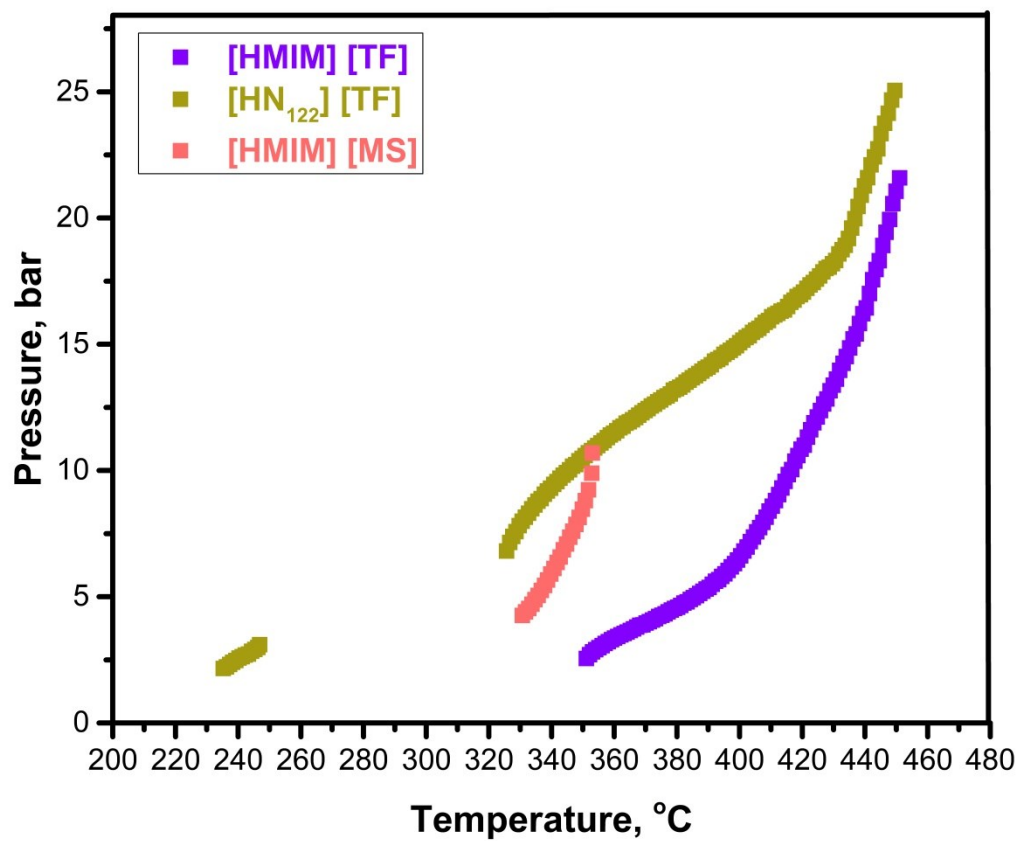
ESI-1 : Temperature vs pressure profiles for protic ionic liquids based on the [Tf]$^-$ and [MS]$^-$ anions.
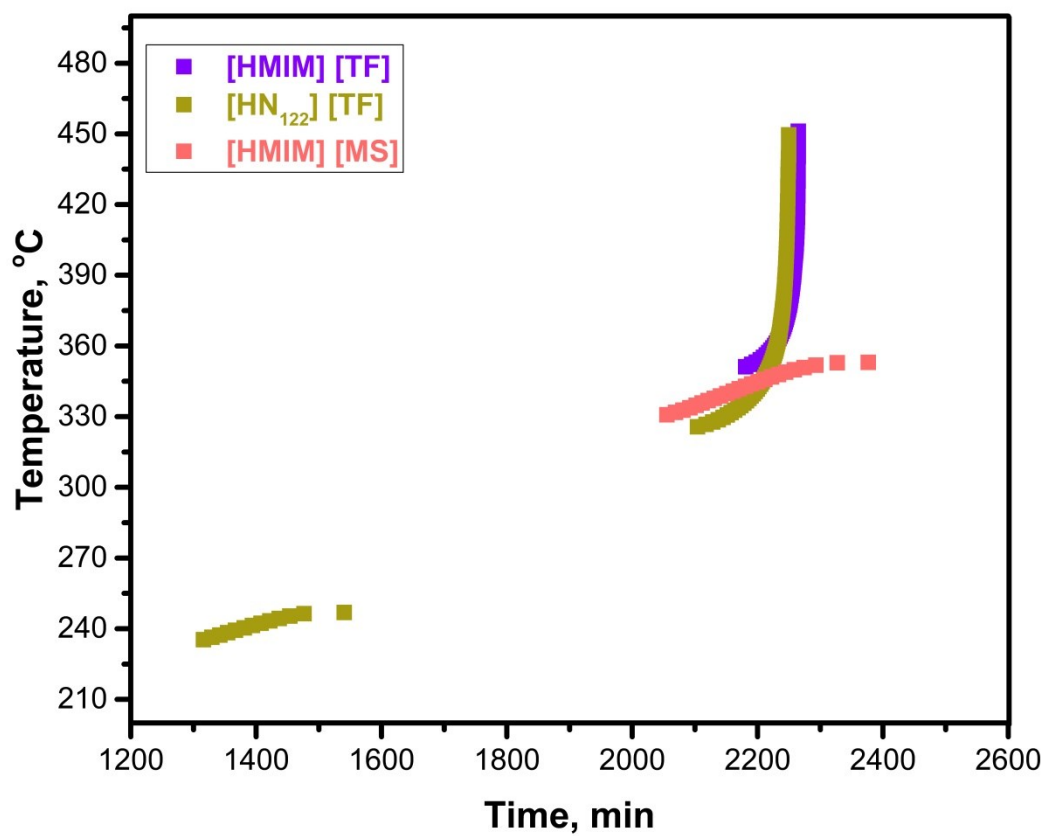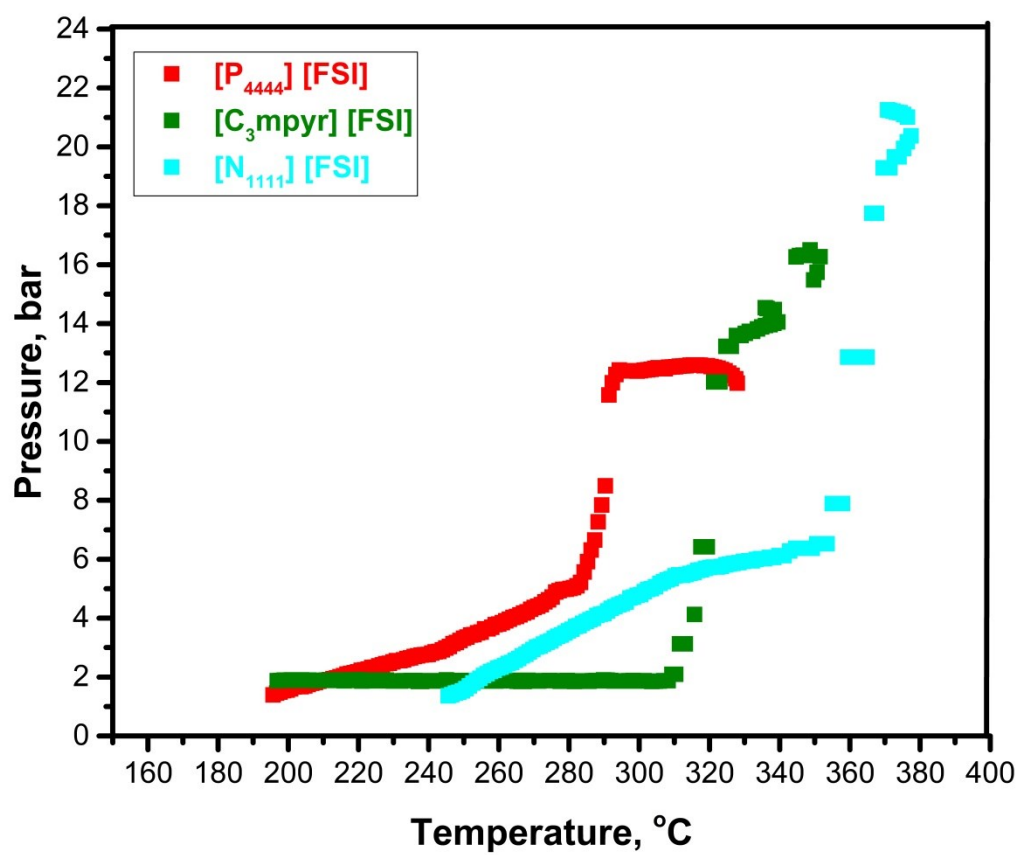
ESI-2 : Time vs Temperature profiles for protic ionic liquids based on [Tf]⁻ and [MS]⁻ anions
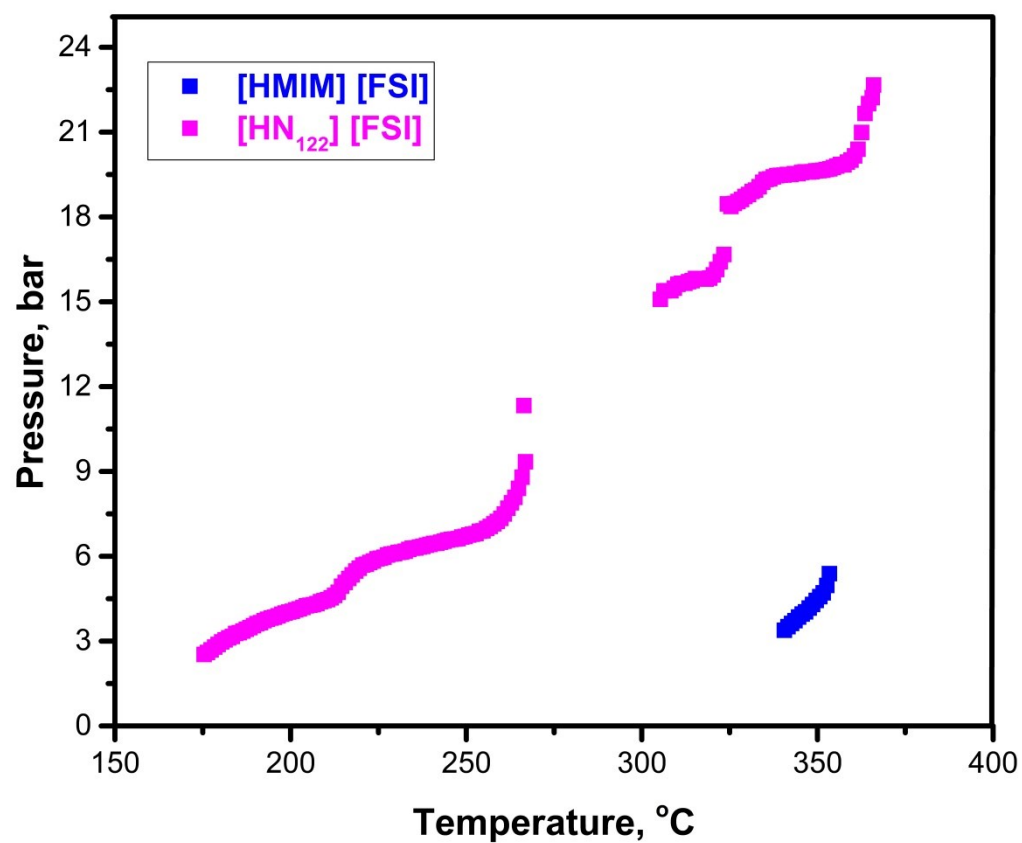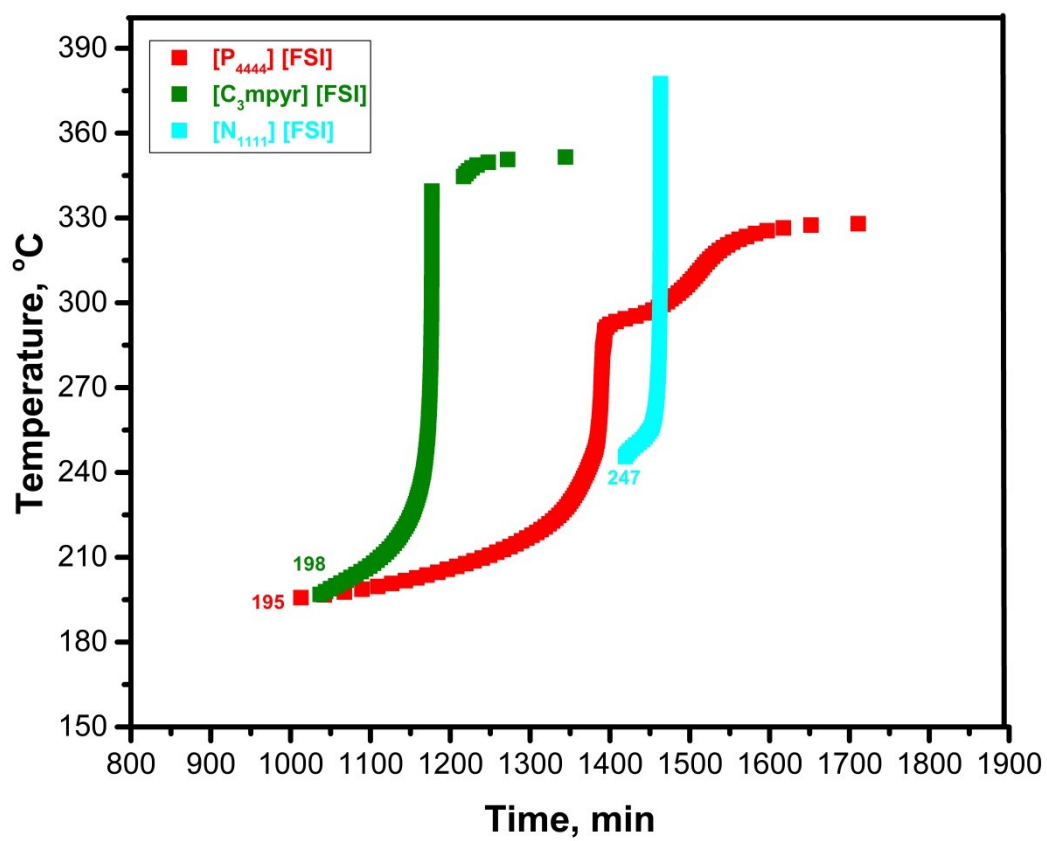
ESI-3 : Temperature vs pressure profiles for protic ionic liquids based on the [FSI]⁻ anion.

ESI-4 : Temperature vs pressure profiles for aprotic ionic liquids based on the [FSI]⁻ anion.

ESI-5 : Time vs Temperature profiles for aprotic ionic liquids based on [FSI]- anion.

Reference

1. M. Surianarayanan, R. Vijayaraghavan, G. Swaminathan and P. G. Rao, *Current Science*, 2001, **80**, 738-747.