

Thermal properties of sulfonic acid group functionalized Brönsted acidic ionic liquids

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Abstract Thermal decomposition onset temperatures have been measured for a total of 24 methylimidazolium, triethanolammonium, and pyridinium type sulfonic acid groups functionalized Brönsted acidic ionic liquids with Cl^- , Br^- , SO_4^{2-} , PO_4^{3-} , BF_4^- , CH_3CO_2^- , and CH_3SO_3^- anions, using thermogravimetric analysis. Thermal stabilities of these sulfonic acid group functionalized ionic liquids decreases in the order, methylimidazolium > triethanolammonium > pyridinium. The methylimidazolium, pyridinium, and triethanolammonium ionic liquids investigated showed decomposition onset temperatures (air) in the 213–353, 167–240, and 230–307 °C ranges, respectively. Additionally, the decomposition temperatures of these ionic liquids are highly dependent on the nature of the anion.

Keywords Acidic ionic liquids · Thermal stability · TG · DTG

Introduction

Ionic liquids have received considerable attention recently for their wide range of applications, which are invariably possible due to attractive physical and chemical properties of these materials [1–5]. These properties include negligible vapor pressure, low inflammability, wide electrochemical window, high inherent conductivity, and liquidity over a wide temperature range, good dissolution ability for a wide variety of organic and inorganic compounds, and good thermal stability. The thermal properties of common

alkyl imidazolium type ionic liquids are the subject of a number of studies in recent times [6–8] as the thermal stability is an important factor in their applications. McEwen has studied [9] the thermal properties of a series of imidazolium and tetralkylammonium salts using thermogravimetric (TG) and scanning differential thermal analyses (SDTA). Ionic liquids with bis-sulfonyl imide anions are shown to be stable up to about 400 °C, whereas the ones with halide anions are shown to have much lower decomposition temperatures of about 300 °C. Furthermore, imidazolium cations are found to be thermally more stable than tetralkylammonium cations. In another study, Kosumulski reported that [10], 1-alkyl-3-methylimidazolium phosphates (alkyl = C4–C10) and 1-decyl-3-methylimidazolium triflate undergoes a slow, but appreciable mass loss even at temperatures as low as 200 °C. On the other hand, 1-butyl-3-methylimidazolium triflate was found to be stable at 200 °C. Burrell has studied [11] the thermal decomposition of ionic liquids, butylmethyl-pyrrolidinium-bis(trifluoromethanesulfonyl)amide and butylmethyl-imidazolium-bis(trifluoromethanesulfonyl)amide by heating up to 250 °C and observing the changes in the UV and fluorescence spectra and reported that colored impurities are formed at temperatures as low as 150 °C, especially when the sample is heated in air.

Functionalized ionic liquids [12–14] are a significant evolution in the ionic liquids area and these materials have been developed for special applications like fossil fuel desulfurization, asymmetric synthesis, preparation of ionic polymers, and as catalysts. In addition to the reaction medium, these smart ionic liquids are typically designed to play a vital second role in the reaction. The sulfonic acid group functionalized Brönsted acidic ionic liquids are a major group in this category and they can play a dual role as the solvent and as an acid catalyst. There are numerous

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applications of using sulfonic acid group functionalized Brønsted acidic ionic liquids as catalysts, which includes esterification [15, 16], alkylation [17], nitration of aromatic compounds [18], Beckmann rearrangement [19], and alkene polymerizations [20]. Our interest in the use of sulfonic acid group functionalized Brønsted acidic ionic liquids in the hydrolysis of lignocellulosic biomass into glucose and fermentable sugars [21, 22] for the cellulosic ethanol production has led us to study the thermal properties of these systems. Additionally, as far as we are aware, there are no reports of systematic studies on the thermal properties of sulfonic acid group functionalized ionic liquid systems. In this communication, we report the thermal properties of a total of 24 imidazolium, triethanolammonium, and pyridinium type sulfonic acid group functionalized Brønsted acidic ionic liquids shown in Fig. 1, studied using TG methods.

Experimental

Sulfonic acid group functionalized Brønsted acidic ionic liquids **1a–h**, **2a–h**, and **3a–h**, shown in Fig. 1 were prepared by condensation of the corresponding nitrogen bases with 1,3-propane or 1,4-butane sultones and then treatment of the salt with the appropriate acid, following the literature procedures [23, 24]. These ionic liquids were purified by repeatedly washing with diethylether and drying under vacuum overnight at 80 °C, then stored in glass vials in a desiccator. 1-*n*-Butyl-3-methylimidazoliumchloride (BMIMCl) was synthesized and purified according to the procedure reported elsewhere [1, 7], and all ionic liquids were characterized by ¹H and ¹³C NMR spectroscopy. The water content of the acidic ionic liquids studied were calculated from TG and found to be less than 1% by weight. We have analyzed the TG curves of the ionic liquids with small variations in the water content, and the decomposition onset temperatures did not show any

significant changes with varying water content. The residual acid was checked by titration of the acidic ionic liquid with standardized 0.054 M sodium hydroxide solution using phenolphthalein as the indicator, and comparing the number of H⁺ ion moles from the titration with the theoretically calculated H⁺ moles of the SO₃H group in the ionic liquid. These experiments showed that there is no residual or excess acid in the acidic ionic liquids used in the study. TG analysis was carried out in nitrogen or in air using TA instruments TGA 2050 system. The mass of the ionic liquid used for a TG scan was approximately 10 mg, and platinum crucibles were used in all experiments. The TG curves were recorded in the 20–600 °C temperature range using a scanning rate of 20 °C/min. The oven was kept at 600 °C for at least 1 h to burn leftovers from the previous run. Temperatures reported from TG data are onset temperatures (T_{onset}), as determined by the step tangent method [9]. The derivative TG analysis (DTG) data are the peaks in the derivative of the weight % curve correspond to weight loss steps in the TG curve.

Results and discussion

Thermogravimetric data for sulfonic acid group functionalized Brønsted acid ionic liquids **1a–h**, **2a–h**, and **3a–h** are shown in the Table 1. Generally, TG and DTG data collected under N₂ atmosphere and air showed small differences, showing that atmospheric oxygen has very little or no role in the decomposition of the sulfonic acid functionalized ionic liquids studied. The decomposition of the Brønsted acidic ionic liquid appears to be not an oxidation reaction and probably an acid catalyzed fragmentation of the ionic liquid structure. In the imidazolium compounds studied, ionic liquids with halide anions showed lower onset temperatures relative to ionic liquids with other anions. For example 1-(1-propylsulfonic)-3-methylimidazolium chloride (**1a**) and 1-(1-propylsulfonic)-3-methylimidazolium bromide (**1b**) showed $T_{\text{onset(air)}}$ values 245 and 241 °C, respectively, whereas the other ionic liquids showed $T_{\text{onset(air)}}$ values in the 288–353 °C range.

Lower decomposition temperatures have been reported for halide anion containing ionic liquids in the neutral alkyimidazolium ionic liquids as well [9]. Additionally, 1-(1-butylsulfonic)-3-methylimidazolium chloride (**1h**) with a four carbon separation between imidazolium ring and the sulfonic acid group showed a lower onset temperature in air (213 °C) compared to **1a** (245 °C) with the three carbon separation between these functionalities. Methylimidazolium (**1a–h**), pyridinium (**2a–h**), and triethanolammonium (**3a–h**) ionic liquids showed decomposition onset temperatures (air) in 213–353, 167–240, and 230–307 °C ranges, respectively. Therefore, in general thermal stability of the sulfonic acid ionic liquids studied

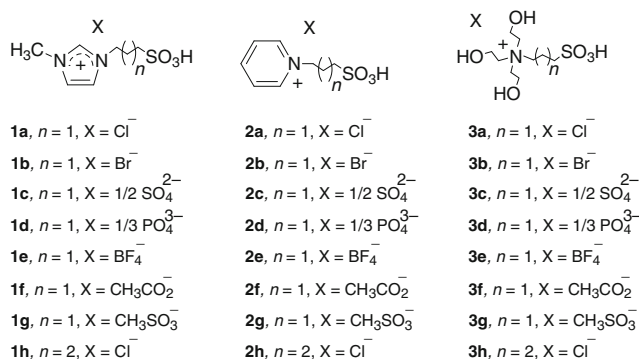


Fig. 1 Sulfonic acid group functionalized Brønsted acidic ionic liquids

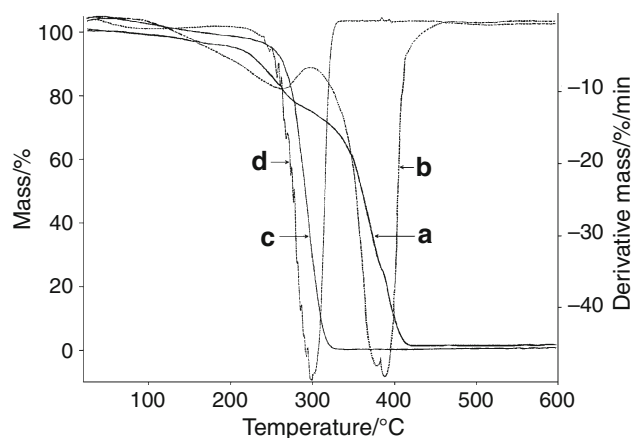
Table 1 Onset temperature (T_{onset}) and derivative thermogravimetric analysis (DTG) peaks data for sulfonic acid group functionalized Brønsted acidic ionic liquids **1a–h**, **2a–h**, and **3a–h**

Ionic liquid	Air		N ₂	
	$T_{\text{onset}}/^{\circ}\text{C}$	DTG/ $^{\circ}\text{C}$	$T_{\text{onset}}/^{\circ}\text{C}$	DTG/ $^{\circ}\text{C}$
1a	245	270, 380, 400	245	270, 380, 397
1b	241	270, 381, 405	242	270, 380, 400
1c	352	391	350	390
1d	344	369	345	370
1e	295	350, 415	295	350, 416
1f	355	380, 404	356	382, 404
1g	288	325, 382, 438	288	325, 380, 440
1h	213	269, 373, 387	215	268, 376, 386
2a	172	225, 265, 327	174	222, 264, 325
2b	167	220, 265, 322	167	227, 261, 327
2c	240	288, 325	240	288, 328
2d	235	260, 280, 324	235	268, 290, 320
2e	207	255, 278, 298	209	260, 277, 300
2f	240	290, 330	241	287, 340
2g	202	254, 272, 289	203	254, 281, 293
2h	174	225, 261, 326	175	227, 261, 327
3a	238	284, 337	240	283, 338
3b	230	280, 336	233	282, 339
3c	307	344, 370	307	344, 375
3d	303	340, 370	306	345, 380
3e	273	315, 365	273	315, 370
3f	307	345, 375	308	344, 372
3g	268	304, 358	269	306, 360
3h	238	282, 334	240	282, 331

decreases in the order, methylimidazolium > triethanolammonium > pyridinium. In the methylimidazolium type sulfonic acid ionic liquid series, the thermal stability of these materials is highly dependent on the anion and decreases in the order $\text{CH}_3\text{CO}_2^- > \text{SO}_4^{2-} > \text{PO}_4^{3-} > \text{BF}_4^- > \text{CH}_3\text{SO}_3^- > \text{Cl}^- > \text{Br}^-$. A somewhat similar trend is found in the pyridinium and triethanolammonium compounds as well, and in these sets of ionic liquids studied, the stability order is: $\text{CH}_3\text{CO}_2^- \sim \text{SO}_4^{2-} > \text{PO}_4^{3-} > \text{BF}_4^- > \text{CH}_3\text{SO}_3^- > \text{Cl}^- > \text{Br}^-$.

All triethanolamine based ionic liquids (**3a–h**) showed only two peaks in the DTG curves, and this may be due to the fact that these ionic liquids, which are the least stable group of the three, decomposes by the same mechanism, independent of the anion associated with the ionic liquid. The relatively more stable imidazolium (**1a–h**) and pyridinium (**2a–h**) ionic liquids shows one to three peaks in the DTG curves showing that their decomposition mechanisms are highly dependent on the nature of the anion.

In order to compare the thermal properties of a sulfonic acid group functionalized acidic ionic liquid with the

**Fig. 2** a TG-**1h**, b DTG-**1h**, c TG-BMIMCl, d DTG-BMIMCl. Thermogravimetric analysis (TG) and derivative TG analysis (DTG) curves for **1h** and 1-*n*-butyl-3-methylimidazolium chloride (BMIMCl) under N₂ atmosphere

corresponding neutral ionic liquid, we have studied the TG curves of **1h** and 1-*n*-butyl-3-methylimidazolium chloride (BMIMCl) under N₂ atmosphere as shown in the Fig. 2. The decomposition onset temperatures for **1h** and BMIMCl calculated using tangent method are 215 and 275 °C, respectively, showing that sulfonic acid functional group in **1h** significantly lowers the thermal stability of the ionic liquid. The DTG curve for BMIMCl indicated one peak at 298 °C, whereas the sulfonic acid functionalized analog **1h** revealed three peaks at 268, 376, and 386 °C. The other sulfonic acid functionalized ionic liquids with halogen anions (**1a,b**) also showed similar three-step decomposition behaviors under N₂ atmosphere or in air as shown in the Table 1.

Conclusions

Generally sulfonic acid group functionalized Brønsted acidic ionic liquids are thermally less stable than their corresponding neutral ionic liquids. In the alkylimidazolium ionic liquid series, the decomposition onset temperatures are in the range of 213–353 °C for the acidic ionic liquids investigated in this study, whereas onset temperatures in the range of 282–470 °C are reported [9] for common neutral alkylimidazolium ionic liquids, indicating their superior thermal stabilities. Acidic ionic liquids with the halogen anions are found to be less stable than compounds with other anions, following the same trend reported for neutral ionic liquids [9]. The pyridinium type acidic ionic liquids are the least stable type, and the thermal stability decreases in the order methylimidazolium > triethanolammonium > pyridinium.

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