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# Auto-ignition characteristics of selected ionic liquids

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**Abstract**

While being compared with commonly used organic solvents, ionic liquids are known of their low volatility. Thus they are usually considered to be green solvents to replace so far used organic solvent to eliminate the pollution of volatile organic compounds. Because of the low volatility, ionic liquids are also considered to be nonflammable in previous studies. However, recent studies do show ionic liquids are flammable. In this study, the auto-ignition characteristics of three ionic liquids, 1-Ethyl-3-methylimidazolium ethylsulfate, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfony)imide, are explored. Auto-ignition temperatures of these three ionic liquids are measured according to ASTM E659 method, and differential scanning calorimeter are used to investigate their thermal decomposition characteristics. Experimental results show that the auto-ignition temperatures of 1-Ethyl-3-methylimidazolium ethylsulfate, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide are 423.1℃, 452.1℃ and 441.5℃, respectively. According to the code of NFPA 70 (National Electrical Code), electric equipment for handling these ionic liquids should meet the requirement of T codes to be T2, T1 and T2 for 1-Ethyl-3-methylimidazolium ethylsulfate, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, respectively. The results of differential scanning calorimeter show that all these three ionic liquids decompose at the temperature below their auto-ignition temperature. It should be noted that the decomposition of 1-Ethyl-3-methylimidazolium ethylsulfate is endothermic, which clearly indicates that the combustion observed at is auto-ignition temperature is the oxidation reaction of the vapors of decomposition products rather than the oxidation reaction of the vapors of ionic liquids itself.



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*Keywords:* Auto-ignition Temperature; Ionic Liquids; ASTM E659 Method

## 1. Introduction

Ionic liquids, which are organic salts that will melt below 100 ℃, are composed of organic cations and inorganic anions. Ionic liquids have the characteristics of relatively low volatility, wide liquids temperature range, and



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nonflammability. Thus, ionic liquids are deemed to be green solvent replacements for the common used volatile organic solvents in part because of aforementioned characteristics [1, 2]. However, recent researches have indicated that ionic liquids are flammable. Fox *et al*. have pointed significant decomposition of ionic liquids does occur at 100 ℃ or much below this temperature [3]. Smiglak *et al*. also indicated that a large group of ionic liquids are combustible due to the nature of their positive heat of formation, oxygen content, and decomposition products [4]. In most countries, the degree of flammability hazard of liquid substance are mainly classified by their flash point. However, Fox *et al*. indicated that although liquids are classified as a flammable liquid or a nonflammable liquid according to their flash point, the flammability hazard of a material should not be defined by a single flammability test [5]. Heat release characteristics of ionic liquids are investigated in their work and they concluded that it would be more appropriate to describe ionic liquids as having low or deduced flammability hazard, rather than identifying as nonflammable materials [5]. The flash point of a combustible substance is usually defined as the temperature, as determined by testing, at which a liquid (or solid) emits sufficient vapour to form a combustible mixture with air [6]. Although the flash points of traditional organic compounds are deemed to be relevant to their vaporization, Liaw et al. have clearly demonstrated that the flash point of ionic liquids is mainly relevant to their decomposition rather than their vaporization [7]. In fact, ionic liquids recently have been classified as a combustible liquid, a class IIIB liquid, by U.S. Occupational Safety and Health Association (OSHA) [5, 8].

Besides flash point and heat release rate, auto-ignition temperature (AIT) is another important characteristic for assessing the flammability hazard of a material. Two common industrial applications of AIT are: (1) determining the required degree of explosion proof for electric equipment operating this combustible liquid; (2) determining the possible consequence associated with leakage of flammable chemicals. For example, article 500.8 of NFPA 70 code provides that "Class I equipment shall not have any exposed surface that operate at a temperature in excess of the ignition temperature of the specific gas or vapour." [9]. Auto-ignition is usually regarded as the ignition of a material commonly in air as the result of heat liberation due to an exothermic oxidation reaction in the absence of an external source such as a spark or flame, and the AIT is then defined as the minimum temperature at which auto-ignition occurs under the specified condition of test [10]. In general, AIT was regarded as the temperature to which a combustible mixture must be raised so that the rate of heat evolved by the exothermic oxidation reactions of the system will just overcome the rate at which heat is lost to the surroundings [11]. Obviously, the ability of a flammable material to spontaneously ignite is an important characteristic for assessing its flammability hazards and such information is indispensable for people who handle, transport, and store such flammable materials. However, although flash points and heat release rates of ionic liquids are explored and discussed recently, the auto-ignition characteristics of ionic liquids are, to authors' best knowledge, never investigated in the literature. In this study, the auto-ignition characteristics of three ionic liquids, 1-Ethyl-3-methylimidazolium ethylsulfate, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, are explored. The other parts of this article are organized as follows. The experimental apparatus, materials, and test procedures are briefly discussed in section 2. Experimental results are summarized and discussed in section 3. Finally, this work is concluded in section 4.

## 2. Experimental section

*Experimental Apparatus and Test Procedure.* Auto-ignition temperature measurements were made on the K47000 auto-ignition apparatus manufactured by the Koehler instrument company. The K47000 instrument is designed to meet the test requirements described by the test method of ASTM E659-78 (2005). The details of experimental procedures could be found in our earlier works [12 - 14]. The thermal stabilities of ionic liquids were determined using a Mettler Toledo 821 Differential Scanning Calorimeter (Switzerland). Samples of 1.0 to 3.0 mg were placed in aluminum pans which is purged with nitrogen at flow-rate of 100 ml/min, and were heated at a scan rate of 10 °C $min^{-1}$. The start temperature and end temperature of the thermal stability analysis are 30 °C and 600 °C, respectively.

*Materials*. All investigated ionic liquids are purchased from commercial companies with guaranteed mass fraction purity. The details of their chemical information are summarized in Table 1, which includes: (1) the molecular formula; (2) the chemical abstract registry number; (3) the guaranteed mass fraction purity; and (4) the supplier. The guaranteed mass fraction purities of 1-Ethyl-3-methylimidazolium ethylsulfate and 1-Hexyl-3-

methylimidazolium bis(trifluoromethylsulfonyl)imide are higher than 99.0%, and that of 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is higher than 98.0%.

Table 1 Chemical information for ionic liquids investigated in this study

| Chemical name | Formula | CAS No. | Mass fraction purity/100 w | Manufacturer |
|---|---|---|---|---|
| 1-Ethyl-3-methylimidazolium ethylsulfate | $C_8H_{16}N_2O_4S$ | 342573-75-5 | 99% | io-li-tec |
| 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | $C_{12}H_{19}F_6N_3O_4S_2$ | 382150-50-7 | 99% | io-li-tec |
| 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | $C_{14}H_{27}N_2{\cdot}C_2F_6NO_4S_2$ | 433337-23-6 | 98% | io-li-tec |

## 3. Results and discussions

Figs. 1−3 show the combustion plots for 1-Ethyl-3-methylimidazolium ethylsulfate, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, respectively. The *x*-axis in these plots is the amount of the sample added into the ignition container, and the *y*-axis is the preheated temperature of the container. If a hot flame was observed in 10 min after the introduction of sample, it was regarded as a flammable case and denoted as a circle in the figure. If the sample was not ignited in 10 min or it generated a cold flame, then it was regarded as a nonflammable case and denoted as a cross. When the sample quantity was purposely varied, the lowest preheated temperature to ignite the sample with a hot flame was also changed. Among these lowest preheated temperatures, the smallest one is, by definition, the AIT and subsequently denoted as a triangle in the combustion plot.

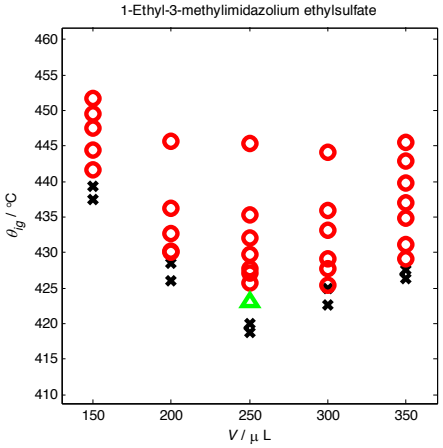


Fig. 1. Ignition temperature (θig) at different sample volumes (V) for 1-ethyl-3-methylimidazolium ethylsulfate: circle, flammable case; cross, nonflammable case; triangle, the lowest flammable temperature.

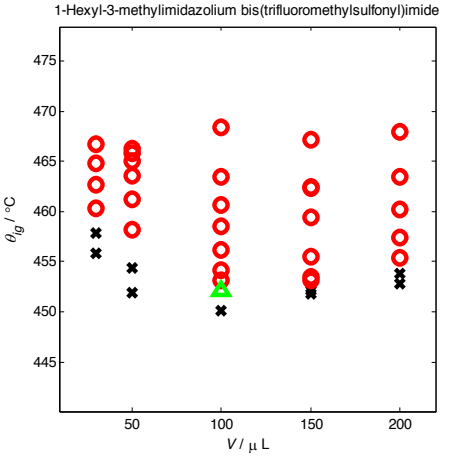


Fig. 2. Ignition temperature (θig) at different sample volumes (V) for 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide: circle, flammable case; cross, nonflammable case; triangle, the lowest flammable temperature.

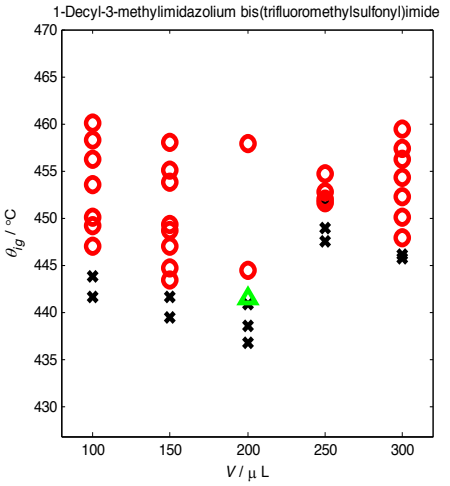


Fig. 3. Ignition temperature (θig) at different sample volumes (V) for 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide: circle, flammable case; cross, nonflammable case; triangle, the lowest flammable temperature.

Table 2 summarizes the measured AITs and the estimates of uncertainty associated with their experimental determination. As previously mentioned, there is a specific sample quantity by which the AIT occurs. If the sample quantity introduced is greater or less than this specific quantity, a temperature higher than the AIT will be required to ignite the compound. This phenomenon is clearly demonstrated in Fig. 1-3. The specific sample quantity corresponding to the AIT for the chemicals investigated in the current study was also tabulated in the third column of Table 2. As it is required by the test report format of ASTM E659 method, the ignition delay time, which is defined as the time lapse between application of heat to a material and its ignition, is also included in the fourth column of Table 2. The T codes, which is the temperature class required for explosion-proof electric equipment to operate these ionic liquids are listed in the last column. It could be observed from table 2 that the ignition delay times of the explored ionic liquids are all about ten seconds, so these ionic liquids should avoid being contacted with hot surfaces of which surface temperature are higher than their individual AIT.

Table 2. Autoignition Temperature ($\theta_{AIT}$), Sample Volume ($V$), Ignition Delay Time ($t_{delay}$) and T code for Ionic Liquids.

| Chemical name | $\theta_{AIT}$ (℃) | $V$(ul) | $t_{delay}$ (sec) | T code |
|---|---|---|---|---|
| 1-Ethyl-3-methylimidazolium ethylsulfate | 423.1 ± 21.16 | 250 | 13.24 | T2 |
| 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | 452.1 ± 22.61 | 100 | 8.24 | T1 |
| 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | 441.5 ± 22.08 | 200 | 9.66 | T2 |

Ionic liquids are usually known of their very low volatility, and this means that the concentration of ionic liquid in vapor phase should be smaller than the lower flammability limit, so it should not be ignited. Thus, it seems interesting to know why they could be ignited in an auto-ignition test. Differential scanning calorimetry (DSC) technique is applied to clarify this issue. Figs. 4 – 6.showthermograms (DSC curves) for 1-Ethyl-3-methylimidazolium ethylsulfate, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, respectively. In these Figures, the $x$-axis is the temperature of the sample pan and the $y$-axis is the power per gram sample added to the reference pan to keep the temperature balance between these two pans. It is clear from these Figures that the decomposition of 1-Ethyl-3-methylimidazolium is endothermic and the others are exothermic. It should be also noted that there are multiple decomposition temperatures for 1-Ethyl-3-methylimidazolium ethylsulfate, and all these decompositions are of endothermic. It could be observed that all auto-ignition temperatures are higher than the corresponding onset temperature, and the AIT of 1-Ethyl-3-methylimidazolium locates behind the temperature of the third decomposition peak.

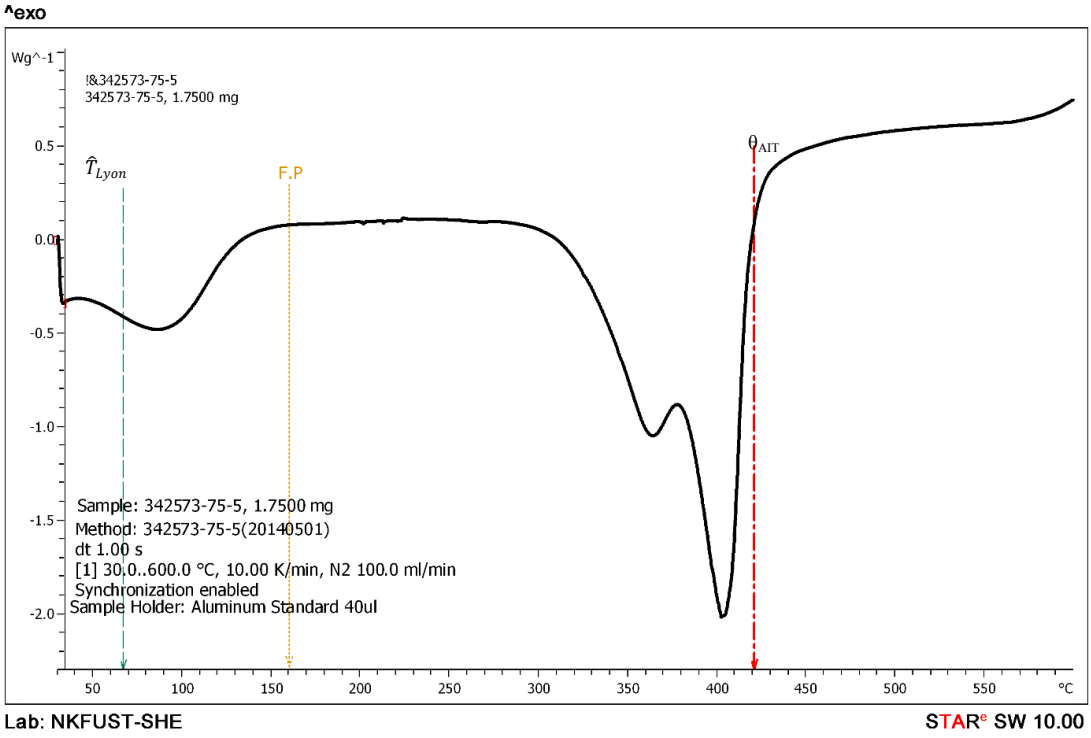


Fig. 4. DSC curve for 1-ethyl-3-methylimidazolium ethylsulfate.

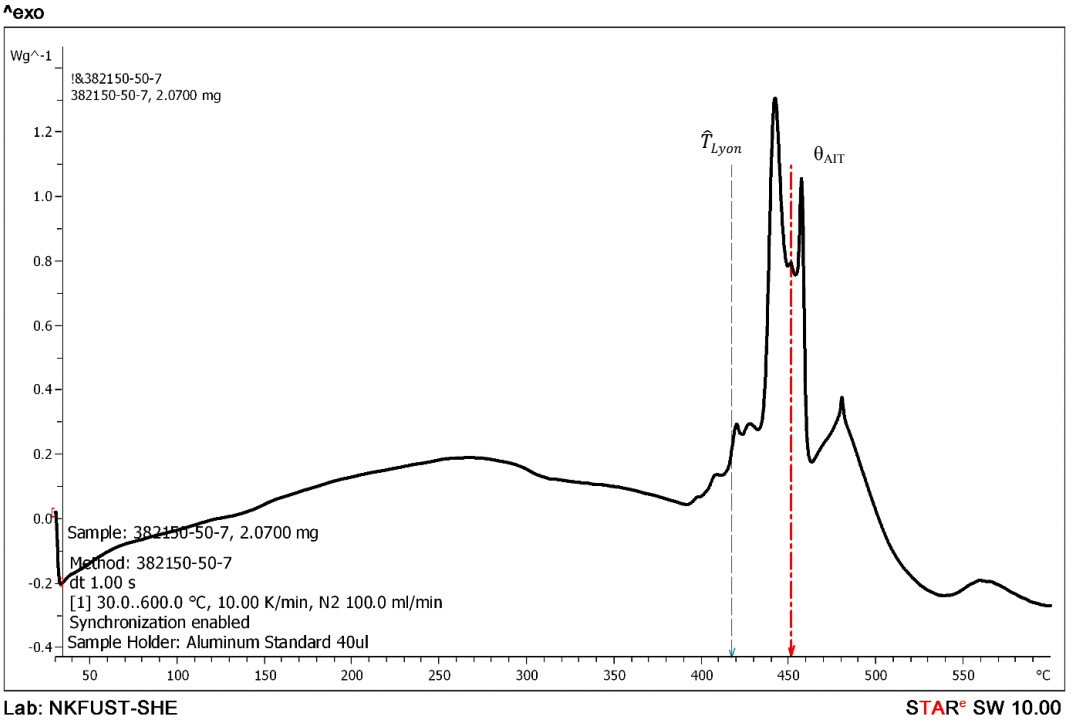


Fig. 5. DSC curve for 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

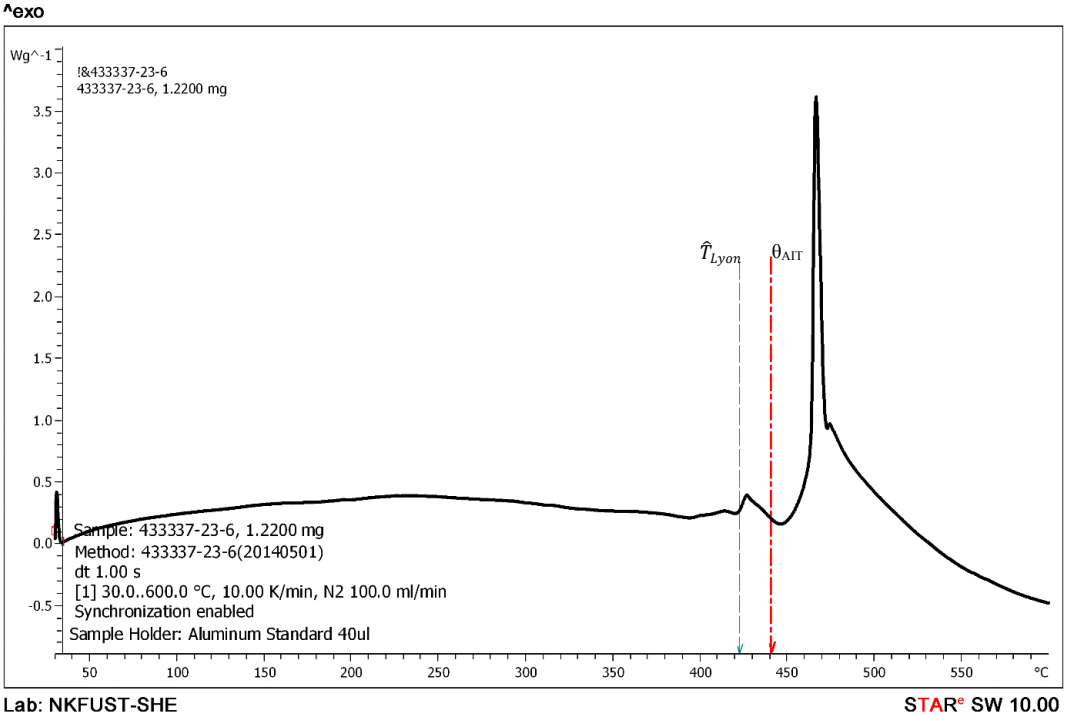


Fig. 6. DSC curve for 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

Table 3 summarizes the onset temperature and peak temperature of DSC curves in Figs. 4-6. For the purpose of later discussions, we include auto-ignition temperature, experimental flash point and the estimated flash point for ionic liquids by Lyon's method in this table. However, because the experimental flash point of 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide are still unavailable in the literature, they are left as blank in the table. As it is shownin Figs. 4-6. The measured auto-ignition temperatures are higher than the beginning decomposition temperature of all explored ionic liquids. Therefore, vapours be ignited at AIT might be vapours of decomposition products rather than vapors of ionic liquid itself. Moreover, as the decomposition of 1-ethyl-3-methylimidazolium ethylsulfate is endothermic, the igniting source should be the ambient temperature rather than heat of decomposition.

Fox *et al*. have suggested that the Lyon's method, which estimates the flash point of polymers by the average of onset temperature and peak temperature in a thermogram, could be used to estimate the flash point of ionic liquid with little overestimation.(3, 5), However, Liaw *et al*. have shown that such an estimation is infeasible for most ionic liquids.(7),The flash point of 1-ethyl-3-methylimidazolium ethylsulfate is also indicated in the DSC curve, and it coincides with Liaw *et al*.'s argument. It seems interesting to note that the estimated temperature by Lyon's method is close to the measured auto-ignition temperature for ionic liquids with exothermic decomposition in present study. However, whether or not this argument holds for general ionic liquids requires more experiments to verify.

Table 3 Onset Temperature ($T_{onset}$), Peak Temperature ($T_{peak}$), Autoignition Temperature ($\theta_{AIT}$), Flash point (FP), Flash point estimated by Lyon's method ($\hat{T}_{Lyon}$)

| Chemical name | $T_{onset}$ (℃) | $T_{peak}$ (℃) | $\theta_{AIT}$ (℃) | FP(℃) | $\hat{T}_{Lyon}$ (℃) |
|---|---|---|---|---|---|
| 1-Ethyl-3-methylimidazolium ethylsulfate | 48.6 | 86.6 | 423.1 | 162* | 67.6 |
| 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | 394.5 | 442.2 | 452.1 | - | 418.3 |
| 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide | 421.8 | 426.3 | 441.5 | - | 424.1 |

* This value of flash point was reported in reference [7]

## 4. Conclusions

In this work, experimental study on the flammable characteristics for three selected ion liquids: 1-Ethyl-3-methylimidazolium ethylsulfate, 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-Decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, are conducted. The measured auto-ignition temperatures for these three ionic liquids are 423.1℃, 452.1℃ and 441.5℃, and the required T codes of NFPA 70 are T2, T1 and T2. The results from DSC curves indicated the combustible vapors may arise from products of decomposition reaction rather than vapors of ionic liquid itself. It is also found that the estimated temperature by Lyon's method is close to the auto-ignition temperature of ionic liquid for explored ionic liquids with exothermic decomposition in present work. However, whether or not this argument holds for general ionic liquids requires more experiments to verify.

**Acknowledgments and Legal Responsibility**

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