Flammability Characteristics of 1-Ethyl-3-Methylimidazolium Bis(Trifluoromethylsulfonyl)Imide

Chan-Cheng Chen, and Jian-He Wu

Abstract—Generally, the fire and explosion hazards of a liquid chemical are classified into two categories: flammability hazard and reactivity hazard. The flammability hazard of a liquid substance primarily depends on the combustibility of its vapor and the reactivity hazard for a chemical refers to the heat released during the reaction. Recently, ionic liquids are considered to be green replacements to so far used organic solvents because of their low volatility. As the flammability hazard of a liquid solvent primarily depends on the combustibility of its vapor, ionic liquids are regarded as nonflammable before. However, recent research indicates ionic liquid could be of flammable hazard.

In this study, the flammability characteristics of ionic liquid 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf$_2$N]) are explored. The auto-ignition temperature of [EMIM][Tf$_2$N] is found to be of 478 °C with an ignition delay time of 12.6 seconds from the auto-ignition temperature tester. Through a TGA/DSC system, a decomposition reaction of [EMIM][Tf$_2$N] is observed at the onset temperature of 300 °C and ends at the temperature of 480 °C. However, the heat effects are different in nitrogen atmosphere and in air atmosphere. The decomposition process in nitrogen atmosphere is endothermic, but it is found to be of exothermic in air atmosphere.

As the decomposition of ionic liquid [EMIM][Tf$_2$N] is endothermic in nitrogen atmosphere, traditional definitions of both flammability hazard and reactive hazard for common liquid solvent seem fail to apply to for [EMIM][Tf$_2$N]. However experimental works in present study do show the decomposition reaction of ionic liquid [EMIM][Tf$_2$N] is exothermic in air atmosphere because of the auto-ignition of the decomposition products. Thus, the ionic liquid [EMIM][Tf$_2$N] should not be considered as a nonflammable substance in general.

Index Terms—Auto-ignition Temperature, Ionic Liquids, ASTM E659 Method.

I. INTRODUCTION

Ionic liquids, which are organic salts that will melt below 100 °C, are composed of organic cations and organic or inorganic anions. Ionic liquids have the characteristics of relatively low volatility, wide liquids temperature range, and nonflammability. Thus, ionic liquids are deemed to be green solvent replacements for the common used volatile organic solvents in part because of aforementioned characteristics [1-4]. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (abbreviated as [EMIM][Tf$_2$N]) is considered to be one of the candidate solvent for surfactants system, and many thermodynamic characteristics of [EMIM][Tf$_2$N] have been thoroughly explored in the literature [3, 4]. However, recent researches have indicated that ionic liquids are flammable, so the flammability concerns of [EMIM][Tf$_2$N] are important to its applicability[5-8].

In most countries, the flammability hazards of liquid solvent are classified according to their flash point, that is, a liquid solvent is classified as a flammable liquid or a nonflammable liquid mainly depends on its flash point. The flash point of a liquid chemical is usually defined as the temperature, as determined by testing, at which the liquid emits sufficient vapor to form a combustible mixture with air [9]. 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 [8]. 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) [10].

In fact, Fox et al. have pointed significant decomposition of ionic liquids does occur at 100 °C or much below this temperature [5]. 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 [6]. As the combustible behaviors of ion liquids are complex, Fox et al. indicated the flammability hazard of ion liquids should not be defined by just a single flammability test of flash point. Heat release characteristics of some 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 [7].

Besides flash point and heat release rate, auto-ignition temperature (AIT) is another important characteristic for assessing the flammability hazard of a material. 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 [11]. 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. The main application of AIT in
process industries is to determine the required degree of explosion proof for electric equipment used to handle this material. 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 vapor.” [12]. Thus, obviously, the ability of a flammable material to spontaneously ignite is an indispensable characteristic for assessing its flammability hazards also.

To make a more understanding of the flammability characteristics of [EMIM][Tf₂N], different technologies are adopted in present work, which includes auto-ignition temperature tester, simultaneous application of Thermogravimetry and differential scanning calorimetry (TGA/DSC). This article is organized as follows. The experimental details including experimental apparatus, materials, and test procedures are described in section 2. Experimental results and discussion are given in section 3. Finally, we concluded this work in section 4.

II. EXPERIMENTAL SECTION

2.1 Materials

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide is commercial merchandise manufactured by the io-li-tec company with guaranteed mass purity of 99%. Table 1 summarizes the basic chemical information of this ion liquid.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Formula</th>
<th>CAS No.</th>
<th>Structural formula</th>
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<tbody>
<tr>
<td>[EMIM][Tf₂N]</td>
<td>C₈H₁₅F₂N₃O₄S₂</td>
<td>174899-82-2</td>
<td></td>
</tr>
</tbody>
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2.2 Experimental Apparatus and Test Procedure

Auto-ignition temperature Tester

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) [11]. The details of experimental procedures could be found in our earlier works [13 – 16].

TGA/DSC

The thermal stabilities of [EMIM][Tf₂N] were determined using a Mettler Toledo TGA/DSC 1. Samples of 1.0 to 3.0 mg were placed in 70µL aluminium oxides pans and were heated at a scan rate of 10 °C min⁻¹. Two atmospheric conditions, nitrogen atmosphere and air atmosphere, are conducted in present work to compare their decomposition behaviour in these atmospheres. The gas is purged at the flow-rate of 50 ml/min in both cases, and the samples are heated from 30 °C to 600 °C in all test runs. This test procedure basically follows the standard of ASTM E537-12[17].

III. RESULTS AND DISCUSSION

The combustion plot of [EMIM][Tf₂N] is shown in figure 1. The x-axis expresses the amount of the sample added into the ignition container, and the y-axis is of the preheated temperature of the container. If a hot flame was observed in 10 min after introducing test sample, it was regarded as a flammable case and denoted as a circle in the figure. If the test sample was not ignited in 10 min or it generated a cold flame, then this case was regarded as nonflammable case with a cross in the figure. 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. The measured AIT of [EMIM][Tf₂N] is found to be of 478 °C, and the corresponding ignition delay time is about 12.6 seconds.

Figure 2 and 3 show the TGA/DSC curves of [EMIM][Tf₂N] in nitrogen atmosphere and air atmosphere, respectively. In nitrogen atmosphere, the TGA curve shows that the decrease of sample weight begins at the temperature of 300 °C, the decrease rate of sample weight drastically increases at the temperature of 430 °C and the decomposition reaction finally ends at the temperature of 480 °C. The DSC curve shows this decomposition reaction is endothermic.

![Fig. 1. Combustion plot of [EMIM][Tf₂N].](image1)

![Fig. 2. The TGA/DSC curves of [EMIM][Tf₂N] in nitrogen atmosphere.](image2)
atmosphere. Sample weight is of 1.983mg. Upper Plot is the TGA curve and the lower plot is the DSC curve. The x-axes in both plots are the temperature (°C) of the test crucible, and the y-axis are the sample percentage (%) remained in the test crucible and heat flux compensated (J/sec) per gram of sample for the TGA and DSC curves, respectively.

In air atmosphere, the TGA curve shows the same trend as the case of nitrogen atmosphere. However, the DSC curve shows entirely different behavior, and obviously exothermic peak, rather than the endothermic peak in nitrogen atmosphere, is found to begins at the temperature of 430°C, although it begins with an endothermic behavior at the temperature of 300°C. Such a phenomenon might indicate that a second decomposition mechanism occurs or the decomposition products are auto-ignited because of the high temperature of the test pan.

The TGA curve and differential thermogravimetry curve (DTG curve) in nitrogen atmosphere and air atmosphere are shown in figure 4 and figure 5, respectively. As it was shown in figure 4, in nitrogen atmosphere, DTA curve is of single peak during the heating procedure, which indicates one decomposition mechanism occurs. The same phenomenon is also observed in air atmosphere, and the onset temperatures in this two cases are the same.

Thus, although the heat effects are not the same for DSC curves in nitrogen and air atmosphere, there decomposition mechanism might be the same. Combing the measured AIT, one possible explanation of the different heat effects in these two cases is the exothermic heat effects in air atmosphere comes from the auto-ignition of the decomposition products.

To further confirm aforementioned conjecture, figure 6 compares the TGA/DSC curves of [EMIM][Tf$_2$N] both in nitrogen atmosphere and air atmosphere with the measured flash point (FP) and AIT. The flash point (FP) of [EMIM][Tf$_2$N] is adopted from a recent reported work and is of 292.3°C [18]. As it could be seen from this figure, the FP roughly locates at the onset temperature of the decomposition and the AIT locates at the end of the decomposition. Thus, it is clearly indicated that the flammability of [EMIM][Tf$_2$N] should be addressed to its decomposition products rather than its vapor. For common liquids, FP is usually deemed to be the temperature at which the vapor concentration of a combustible liquid reaches the lower flammability limit, and then the vapor is ignited by an external spark source. However, it is not the case for the FP of [EMIM][Tf$_2$N]. Traditionally, we also take it for granted that the vapors of a combustible liquid is what we burnt in the test for measuring AIT, but this might be not true either from the observations in figure 6.

IV. CONCLUSIONS

In this work, flammability characteristics of [EMIM][Tf$_2$N] are examined. Auto-ignition temperature tester is used to measure the AIT of [EMIM][Tf$_2$N]. TGA/DSC system are used to test the decomposition behavior of [EMIM][Tf$_2$N] during the programmed temperature process. The AIT of [EMIM][Tf$_2$N] is found to be of 478°C with an ignition delay time of 12.6 seconds. The experimental TGA curve indicates that the
decomposition reaction begins at the temperature of 300°C, the sample weight drastically changes at the temperature of 430°C and the reaction finally ends at the temperature of 480°C. The decomposition heat effects of [EMIM][Tf$_2$N] are different in nitrogen atmosphere and air atmosphere. The decomposition process in nitrogen atmosphere is endothermic, but it is found to be of exothermic in air atmosphere through the TGA/DSC system and the DSC curve indicates that the heat effects begin to be exothermic at the temperature of 430°C. This indicates the effect of heat released in air atmosphere might come from the auto-ignition of the decomposition products in the vapor phase.

Generally, we classify the fire and explosion hazards of a chemical into two categories: flammability and reactivity. The flammability of a liquid substance primarily depends on its flash point which is correlated with combustibility of its vapor. If the fire and explosion hazard of a substance comes from its reaction, this usually refers to the reactivity hazard. However, the reactivity hazard of a chemical is defined for the exothermic reaction [19, 20]. As [EMIM][Tf$_2$N] is a liquid of very low volatility, the traditional definition of the flammability for the common solvent seems fail to apply to [EMIM][Tf$_2$N], because the flash point of [EMIM][Tf$_2$N] does not come from the combustibility of its vapor. Moreover, the common definition of reactivity for common solvents also fails to apply, because the decomposition reaction in nitrogen atmosphere is indeed endothermic. However, the decomposition products of [EMIM][Tf$_2$N] might be auto-ignited near the end of decomposition reaction, and this make the whole reaction to be exothermic. Thus, the ionic liquid [EMIM][Tf$_2$N] should not be considered as a nonflammable substance in general.

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[10] http://dx.doi.org/10.1021/ic800665u