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Thermal stabilities of di-alkylimidazolium chloride ionic liquids

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Abstract

Thermal stability of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-hexyl-3-methylimidazolium chloride ([HMIM]Cl) ionic liquids was investigated using thermogravimetric analysis (TGA). The long-term isothermal TGA studies have revealed that both the ionic liquids exhibit appreciable decomposition at temperatures significantly lower than indicated by the peak or onset decomposition temperature (T_{onset}) determined from fast scan TGA experiments. The long-term thermogravimetric studies of both the ionic liquids showed linear weight loss as a function of time at each temperature of 10 °C interval in the range 150–170 °C over a period of 15 hours. However, the linear weight loss regime decreased with increasing temperature for the range 180–200 °C. The kinetics of isothermal decomposition of ionic liquids was analyzed using pseudo-zero-order rate expression. Arrhenius activation energy for the decomposition of di-alkylimidazolium chloride ionic liquids in the range 150–200 °C was determined.

Keywords: Ionic liquids; Long-term thermal stability; 1-butyl-3-methylimidazolium chloride; 1-hexyl-3-methylimidazolium chloride

Introduction

Room temperature ionic liquids are salts that are composed entirely of ions [1]. Room temperature ionic liquids (RTILs) are commonly defined as salts with melting temperature below the boiling point of water [2]. RTILs have received immense attention because of their unique chemical and physical properties viz., high thermal stability, low melting point, negligible vapor pressure, high thermal conductivity and wide electrochemical window [1]. In the last two decades there has been extensive research in synthesizing new RTILs due to their potential to replace many volatile organic chemical solvents (VOCs). RTILs are extensively investigated for application in various technological fields such as solar cell applications, electrochemical capacitors, batteries, catalytic applications, extraction processes, and metal deposition [3–6]. The physical and chemical properties of several RTILs are thoroughly investigated due to their expanding scope of applications. However, systematic studies quantifying the purity, stability, biodegradability, and toxic-

ity of ionic liquids have lagged behind the pace of other research [7].

Halide based salts are the most widely studied class of room temperature ionic liquids. Moreover, halide based salts are precursors for several air and water stable RTILs, e.g., numerous di-alkylimidazolium based ionic liquids (C_nMIMPF$_6$, C_nMIMBF$_4$, C_nMIMTf$_2$N, etc.) are synthesized from di-alkylimidazolium chlorides. The mixture of di-alkylimidazolium chloride ([R$_1$R$_2$IM]Cl) and AlCl$_3$, which are termed as chloroaluminate ionic liquids, have been extensively studied for metal/alloy deposition and transition metal catalysis. Physical and chemical properties of several di-alkylimidazolium chlorides were reported in the literature [8,9]. Standard enthalpy, entropy, Gibbs energy change and heat capacity of di-alkylimidazolium chloride ionic liquids were also investigated [10,11].

Ionic liquids were considered non-volatile until Earle et al. [12] reported that some ionic liquids are volatile, and can be distilled. The first-generation ionic liquids were believed to be non-volatile since the earlier reports on vapor pressure studies of 1-methyl-3-ethylimidazolium chloride – aluminum chloride [13]. Numerous studies exploiting the high thermal stabilities of ionic liquids were based on the assumption that IL's exhibit negligible vapor pressure. However, the recent studies

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revealed the volatile nature of some IL's at temperatures below their decomposition and mild pressure, creating an opportunity for separating ionic liquids by distillation [12]. Ionic liquids were recycled by distillation and recombination of 'partial-decomposition' products generated upon heating under reduced pressures [14]. Vapor pressure is another physical–chemical property that depends on an ionic liquid's cation-anion combination and will in future have to be checked experimentally for each ionic liquid [15]. Moreover, the volatile nature of ionic liquids makes the evaluation of thermal properties critical for their practical applications.

Thermal stability is a significant factor that determines the applicability of ionic liquids for high temperature applications. Onset decomposition temperature of several ionic liquids determined using scanning TGA method was reported [16–18]. Zhang et al. [19] have investigated long-term isothermal stabilities of $[C_4mim][Tf_2N]$, $[C_6mim][PF_6]$ and $[C_8mim][PF_6]$ and it was observed that these IL's decompose at a faster rate with increasing temperature. Baranyai et al. [20] have reported that ionic liquids yield volatile products at temperatures significantly lower than the onset-decomposition temperature. The onset decomposition temperatures obtained using scanning TGA studies are overrated and true stability temperature is lower than the later [21–23]. Hence, the stable temperature limit of ionic liquids is not precisely defined by the onset-decomposition temperature. Scarcity of reliable long-term thermal stabilities of di-alkylimidazolium chloride ionic liquids leads to the current research. The present study reports the long-term thermal stabilities and kinetics of isothermal decomposition of [BMIM]Cl and [HMIM]Cl ionic liquids.

Experimental procedure

Di-alkylimidazolium chloride ([BMIM]Cl and [HMIM]Cl) ionic liquids were synthesized and purified according to the procedure reported elsewhere [1]. Raw materials for synthesizing di-alkylimidazolium chloride such as 1-methylimidazole (>99%), 1-chlorobutane (>99.5%), 1-chlorohexane (>99.5%) and ethyl acetate (99.8%) were purchased from Sigma Aldrich®. The final product ionic liquids were purified using an indigenously built vacuum evaporation system. The vacuum evaporation was performed at 70 °C for 12 hrs using a vacuum pump (Welch Vacuum®, Gem Vacuum Pump). 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) was colorless liquid, which solidified into a white crystalline solid on cooling to room temperature. 1-hexyl-3-methylimidazolium chloride ([HMIM]Cl) was a light yellow liquid.

Ionic liquids were characterized qualitatively for purity by NMR spectroscopy and moisture content using Karl Fischer titration method. The NMR spectrum results for [BMIM]Cl are as follows: ^{1}H NMR (DMSO, ppm) results: δ 0.84(t), 1.20 (sextet), 1.74(q), 3.88(s), 4.21(t), 7.88(s), 7.97(s), 9.74(s). ^{13}C NMR (DMSO, ppm): δ 13.16, 18.64, 31.32, 35.58, 48.23, 122.21, 123.44, and 136.75. NMR spectrum results for [HMIM]Cl are as follows: ^{1}H NMR (CDCl$_3$, ppm) results: δ 0.14(t), 0.59(sextet), 1.20(q), 3.44(s), 3.65(t), 7.04(s), 7.21(s), 9.72(s). ^{13}C NMR (CDCl$_3$, ppm): δ 12.44, 20.82, 24.32, 28.32, 28.74, 29.55,

35.02, 48.40, 76.73, 76.99, 77.25, 120.88, 122.54, and 135.81. Moisture content was determined using Karl Fischer titrator (Aquapal III, CSC Scientific®) with Hydranal C as titrant and Hydranal A reagent as solvent. The moisture content of [BMIM]Cl and [HMIM]Cl is 0.18 and 0.08 wt% (dried), respectively. The purity of ionic liquids synthesized is typical of the commercially available ionic liquids.

Perkin Elmer® Pyris Diamond TG/DTA was used to perform thermogravimetric analysis of ionic liquids. TG/DTA instrument uses two horizontal balance beams. Alumina pans were used for both sample and reference material. α-Al$_2$O$_3$ powder was used as the reference material for all the experiments. The instrument was calibrated for the temperature range 25 to 1100 °C using indium, tin and gold standard samples provided by Perkin Elmer®. A constant heating rate of 10 °C/min and argon gas purging at a flow rate of 150 mL/min was used for all the experiments. Isothermal thermogravimetry was performed at a constant temperature for 15 hours (arbitrary choice). Measurements were carried out at each temperature of 10 °C interval in the temperature range 150–200 °C. The sample weights used for thermogravimetric analysis were in the range 15–18 mg for [BMIM]Cl and 35–40 mg for [HMIM]Cl. Since [HMIM]Cl is liquid at room temperature, typically a drop of the liquid was used as a sample.

Results and discussion

Long-term thermal stability

The long-term thermal behavior of [BMIM]Cl and [HMIM]Cl ionic liquids was investigated using isothermal TGA studies for 15 hours with argon purge at 150 mL/min. Long-term TGA studies of [BMIM]Cl ionic liquid at different temperatures are shown in Fig. 1. A linear weight change with time is observed at each temperature of 10 °C interval in the range 150–170 °C, whereas the linear weight change regime was not observed for the entire duration for temperatures in the
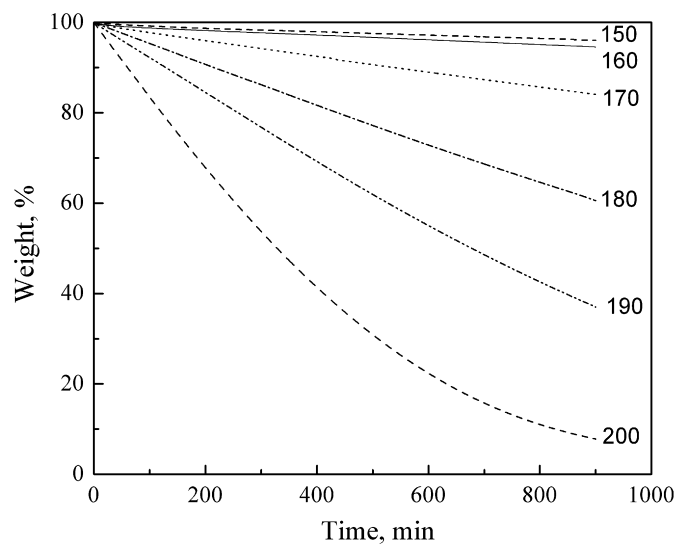

Fig. 1. Isothermal thermogravimetry of [BMIM]Cl at different temperatures in argon purge (150 mL/min). Temperatures shown in the figure are in centigrade.
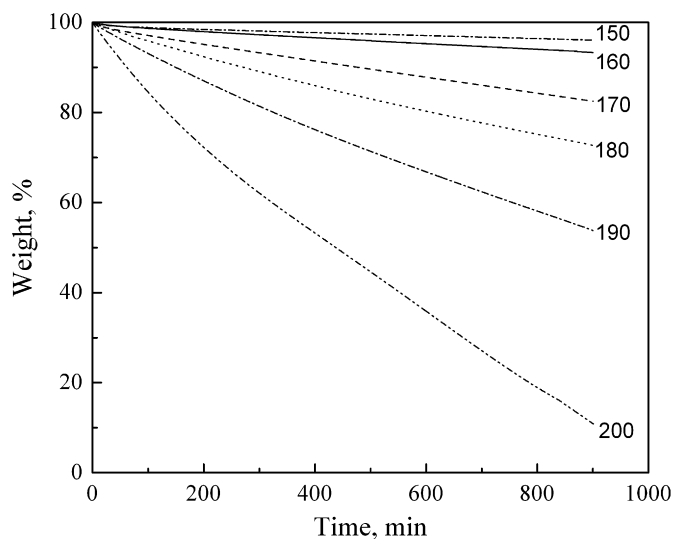
Fig. 2. Isothermal thermogravimetry of [HMIM]Cl at different temperatures in argon purge (150 mL/min). Temperatures shown in the figure are in centigrade.
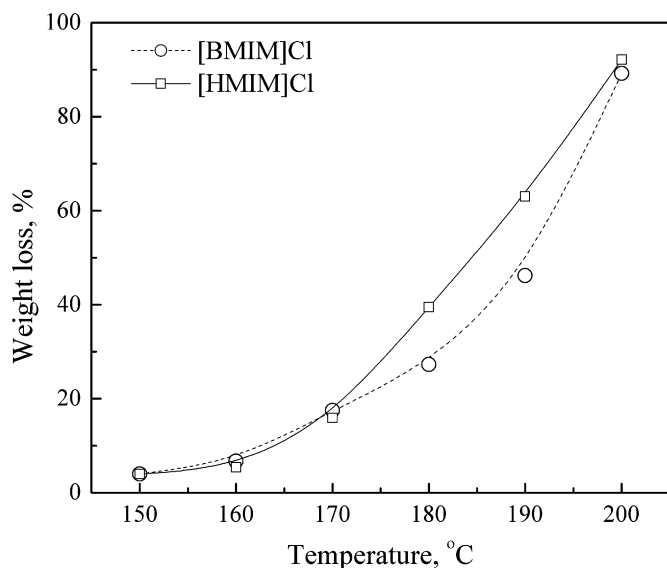

Fig. 3. Variation of weight loss of di-alkylimidazolium chloride ionic liquids as a function of temperature after 15 hours of isothermal thermogravimetry.

range 180–200 °C. Moreover, the linear weight change regime decreased with temperature, e.g., linear weight change was observed for about 200 min at 200 °C. Similarly, the progressive weight change of [HMIM]Cl ionic liquid at each temperature of 10 °C interval in the range 150–200 °C is illustrated in Fig. 2. As observed previously, linear weight change was observed for the temperatures in the range 150–170 °C for 15 hours. Linear weight change regime for temperatures in the range 180–200 °C was observed for about less than 500 min.

The comparison of weight loss of both the ionic liquids as a function of temperature after 15 hours of isothermal thermogravimetry is demonstrated in Fig. 3. Weight loss increased gradually in the temperature range 150–170 °C, thereafter it increased rapidly with temperature (170–200 °C). The weight loss of about 20 pct is observed for the range 150–170 °C which is less compared to that observed in the range 180–200 °C. Ap-

proximately similar weight loss is observed for both the ionic liquids at all temperatures within experimental errors. Based on the current results it is observed that di-alkylimidazolium chloride ([BMIM]Cl and [HMIM]Cl) ionic liquids exhibit substantial (15 h) long-term thermal stability up to 160 °C with less than 10 pct weight loss. The onset decomposition temperature determined for both the ionic liquids using the fast-scan TGA method is useful to serve as the limiting value for their practical applications. However, from the current study, it was observed that di-alkylimidazolium chloride ([BMIM]Cl and [HMIM]Cl) ionic liquids lose weight progressively when heated at elevated temperature (>160 °C) for a long time. Several studies have reported similar results on other di-alkylimidazolium ionic liquids in the literature [20–22].

Decomposition of imidazolium salts is attributed to decomposition of cation as facilitated by the anion which itself becomes transformed [24]. Pyrolysis of imidazolium salts yielded volatile degradation products such as 1-alkylimidazoles and alkylated anions and the degradation pathway was identified as E2 elimination of the N-substituent, which is essentially the reverse of SN2 substitution synthesis reaction [25]. Nucleophilicity of anion and the ability of cation to undergo alkylmigration or elimination reaction have a significant influence on thermal stability of ionic liquids [17,20]. Moreover, halide based imidazolium salts exhibit poor thermal stabilities.

Kinetics of isothermal thermogravimetry

The isothermal TGA studies were used to analyze the kinetics of decomposition of di-alkylimidazolium chloride ionic liquids. As portrayed in Figs. 1 and 2 the weight change with time (initial linear regime for 180–200 °C) is linear, hence the rate of decomposition (rate of weight change) at a temperature is constant. Since the rate of decomposition of ionic liquids depend on mass and heat transfer rather than on chemical reaction, a pseudo-zero-order rate expression is used to determine the decomposition kinetics [20,21]. The rate expression at a constant temperature can be represented as follows:

$$\frac{d\alpha}{dt} = k \qquad (1)$$

where k is the pseudo-zero-order rate constant and α is the degree of conversion. The degree of conversion (α) is defined as shown in Eq. (2), where W_t is the weight of sample at a time t and W_i is the initial weight.

$$\alpha = \frac{(W_i - W_t)}{W_i} \qquad (2)$$

The rate expression in Eq. (1) can be represented in integral form as shown in Eq. (3), where t is time and C is a constant.

$$\alpha = kt + C \qquad (3)$$

Accordingly, the degree of conversion (α) as a function of time was determined for both the ionic liquids from their respective weight change versus time plots (Figs. 1 and 2). Similar to that mentioned in the previous section, the α vs. t plots for both the ionic liquids were linear for the entire duration (15 h) for 150–170 °C and for the range 180–200 °C linear regime is
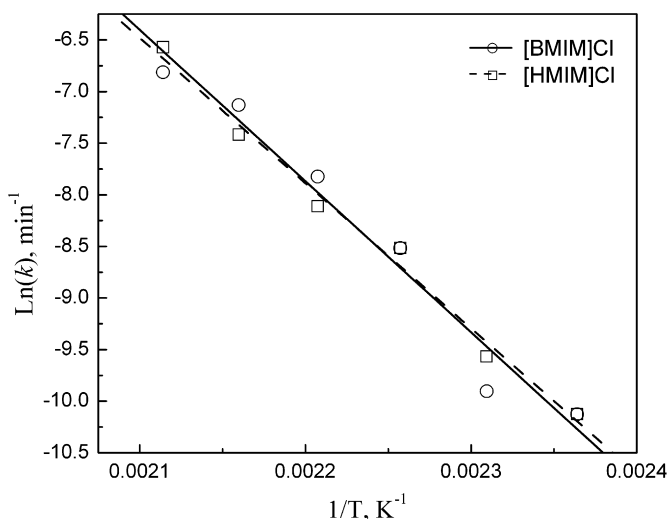
Fig. 4. Arrhenius plot [$\ln k$ vs. $1/T$] for the decomposition of di-alkylimidazolium chloride ionic liquids in the temperature range 150–200 °C (argon purge).

observed only initially. Hence, initial linear portion of the plots (α vs. t) for the range 180–200 °C were considered for further calculations.

The pseudo-zero-order rate constant is determined at different temperatures from the slope of linear portion of α vs. t plots. The temperature dependence of pseudo-zero-order rate constant (k) is expressed by Arrhenius relation as follows:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \qquad (4)$$

where E_a is Arrhenius activation energy and A is pre-exponential coefficient. Fig. 4 illustrates the Arrhenius plot [$\ln k$ vs. $1/T$] for [BMIM]Cl and [HMIM]Cl ionic liquids. Activation energy is determined from the slope of Arrhenius plot and intercept of the plot yields pre-exponential coefficient (A). Activation energy for the decomposition of [BMIM]Cl and [HMIM]Cl in the temperature range 150–200 °C (with argon purge) are 121 and 117 kJ, respectively. The pre-exponential coefficients for [BMIM]Cl and [HMIM]Cl are 3.8×10^{10} min^{-1} and 1.0×10^{10} min^{-1}, respectively.

Conclusions

The long-term isothermal TGA studies have revealed that both [BMIM]Cl and [HMIM]Cl ionic liquids exhibit appreciable decomposition at temperatures significantly lower than the peak or onset decomposition temperature (T_{onset}) determined using fast-scan TGA. The isothermal TGA studies showed that [BMIM]Cl and [HMIM]Cl ionic liquids have substantial (15 h) long-term thermal stability up to 160 °C. A pseudo-zero-order rate law was employed to determine the kinetics of isothermal decomposition of ionic liquids in the temperature range of 150–200 °C. Activation energies for decomposition of [BMIM]Cl and [HMIM]Cl determined using Arrhenius relation are 121 and 117 kJ, respectively.

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