Thermokinetics of SO$_3$H-functionalized dicationic ionic liquids: Effect of anions

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Abstract. In this study, the kinetics of thermal degradation of three ionic liquids (ILs) were investigated using non-isothermal thermogravimetric analysis to investigate the thermal stability of ILs with various anion. Di(4-sulfonic acid) dibutyltriethylene diammonium di(hydrogen sulfate, ([DABCODBS][HSO$_4$]$_2$), di(4-sulfonic acid) dibutyltriethylene diammonium di(trifluoromethanesulfonate) ([DABCODBS][CF$_3$SO$_3$]$_2$ and di(4-sulfonic acid) dibutyltriethylene diammonium di(chloride) ([DABCODBS][Cl]$_2$) were subjected to thermogravimetric analysis (TGA) in the temperature range of 50-800°C at four heating rates of 10, 15, 20 and 25°C/min using nitrogen at a flow rate of 20 L/min as purge gas. The average activation energies ($E_a$) calculated using Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (FWO) and Starink methods are 163.49, 173.33 and 162.58 kJ/mol for [DABCODBS][HSO$_4$]$_2$, 119.59, 130.41 and 119.07 kJ/mol for [DABCODBS][CF$_3$SO$_3$]$_2$ and 199.72, 210.50 and 198.63 kJ/mol for [DABCODBS][Cl]$_2$, respectively. The results presented through all kinetic methods are in close agreement with each other and showed a decreasing thermal stability trend of [DABCODBS][Cl]$_2$ > [DABCODBS][HSO$_4$]$_2$ > [DABCODBS][CF$_3$SO$_3$]$_2$. The results also showed that intermediates were formed for [DABCODBS][Cl]$_2$ and [DABCODBS][HSO$_4$]$_2$ until achieved total decomposition, while there was no intermediate formed for the pyrolysis kinetic of [DABCODBS][Cl]$_2$. This study shows the effect of nature of anion towards the thermal stability and decomposition mechanism of ILs.

1. Introduction

Ionic liquids (ILs) have become an attractive candidate as effective and environmental-friendly materials investigated in the last decade. ILs are molten salts in liquid form at temperature below 100°C [1] and are composed of a cation and an anion [2]. Their properties can be tuned by combination of organic cations with various inorganic or organic anions. Through these combination, a large amount of salts can be synthesized for numerous possible applications [3,4]. Their remarkable physicochemical properties such as high thermal stability and negligible vapor pressure solved the issue related to volatility and flammability [5,6]. They are reviewed as prospective materials due to their inherent characteristics such as being less corrosive, ease of separation, recyclable, applicable for continuous process and less production of waste water. Therefore, the number of reactions and purification steps could be reduced [7,8]. Their distinctive properties encouraged their application as heat transfer fluids, lubricants, propellants, solvents, catalyst and additives [9,10]. However, these applications are often implemented in high temperature condition. This may result to decomposition of
materials which lead to significant hazard cause by gas generation, inflammation and rapid detonation [11]. Therefore, it is essential to study the thermal behavior and degradation temperature of ionic liquids for commercial scales application at wide temperature range [12]. ILs thermal stability can be affected by several factors such as structure of cation and anion, length of alkyl chain, functional group and impurities [13,14]. Hence, several techniques have been applied to assess the thermal stability of materials. Among them, thermogravimetric analysis technique is often used for its simplicity. The thermogravimetric analysis technique can be classified into several groups such as ramping technique, isothermal technique and isoconversional technique (integral, differential and incremental) [9,15]. Through these techniques, the activation energy can simply be calculated through Kissinger-Akahira-Sunose (KAS) [16], Flynn-Wall-Ozawa (FWO) [17,18] and latest Starink [19] methods. These methods also allow determination of the chemical steps of the degradation process and kinetic parameters for each step. The kinetic parameters can be calculated using the thermogravimetric (TG) curve of various heating rate under nitrogen or air flow [20]. In ILs field, this thermokinetic study has just recently being explored for a better understanding on the thermal stability of ILs. Such study includes exploration on thermal stability of ILs of various cations such as imidazolium [21,22], benzyimidazolium [23], pyrrolidinium [13,24,25], piperidinium [12] and phosphonium [13]. However, the exploration on thermal properties and kinetic parameters covered only limited ILs. The effect of structure of cation and anion towards the thermokinetics behavior has yet to be compared in a single study. In our previous study, we have reported DABCO based ILs as potential catalysts for production of biodiesel [10]. In this present work, isoconversional thermal analysis were conducted to evaluate the thermal stabilities of the three DABCO-based ionic liquids with variety of anions, namely di(4-sulfonic acid) dibutyltriyethylene diammonium di(hydrogen sulfate), ([DABCODBS][HSO₄]), di(4-sulfonic acid) dibutyltriyethylene diammonium di(trifluoromethanesulfonate) ([DABCODBS][CF₃SO₃]), and di(4-sulfonic acid) dibutyltriyethylene diammonium di(chloride) ([DABCODBS][Cl]). The kinetic parameters were determined by three isoconversional methods including KAS, FWO and Starink methods.

2. Experimental

2.1. Reagents and materials

All chemicals were commercially available. They were used without further purification unless otherwise stated. ¹H NMR spectra were recorded on a Bruker 400MHz spectrometer using D₂O as solvent.

2.2. Synthesis of ionic liquids

1,4-diabazicyclo[2,2,2]octane (DABCO) was reacted with 1,4-butane sulfone in ethanol as solvent at 55°C for 3 days, forming white precipitate. The precipitate was then filtered, washed with solvents and dried. The white powder product was the zwitterion precursor. Double equivalent of sulphuric, trifluoromethanesulfonic and hydrochloric acid were also reacted on the same zwitterion precursor. After that, the product was dried to remove water, giving solid ILs at ambient temperature. The structure of the ILs were shown in Figure 1. a) Di(4-sulfonic acid) dibutyltriyethylene diammonium di(hydrogen sulfate), ([DABCODBS][HSO₄])

¹H NMR (δ, ppm): 1.74 (m, 2×2H), 1.92 (m, 2×2H), 2.89 (t, 2×2H), 3.53 (t, 2×2H), and 3.92 (s, 6×2H), b) Di(4-sulfonic acid) dibutyltriyethylene diammonium di(trifluoromethanesulfonate), ([DABCODBS][CF₃SO₃]),

¹H NMR (δ, ppm): 1.74 (m, 2×2H), 1.92 (m, 2×2H), 2.89 (t, 2×2H), 3.53 (t, 2×2H), and 3.92 (s, 6×2H), c) Di(4-sulfonic acid) dibutyltriyethylene diammonium di(chloride), ([DABCODBS][Cl])

¹H NMR (δ, ppm): 1.75 (m, 2×2H), 1.93 (m, 2×2H), 2.91 (t, 2×2H), 3.55 (t, 2×2H), and 3.93 (s, 6×2H).
2.3. Thermokinetic study

The thermal behaviour of ILs was measured using Perkin-Elmer, Pyris V-3.81 thermal gravimetric analyser (TGA). The samples were placed in sealed aluminium pan under nitrogen flow of 20 L/min in the temperature range of 50-800°C at four heating rate of 10, 15, 20 and 25°C/min. The kinetic parameters was determined based on the data of thermogravimetric graphs following the approach of Kissinger-Akahira-Sunose (KAS) method, Flynn-Wall-Ozawa (FWO) method and Starink method. These methods were mathematically expressed by equation (1), (2) and (3) for KAS, FWO and Starink methods, respectively.

\[
\text{Kissinger-Akahira-Sunose (KAS) method: } \ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{E_a g(\alpha)} \right) - \frac{E_a}{RT} \tag{1}
\]

\[
\text{Flynn-Wall-Ozawa (FWO) method: } \ln \beta = \ln \left( \frac{AE_\alpha}{Rg(\alpha)} \right) - 5.331 - \frac{1.052E_\alpha}{RT} \tag{2}
\]

\[
\text{Starink method: } \ln \left( \frac{\beta}{T^1.92} \right) = \ln \left( \frac{AE^{0.92}_\alpha}{g(\alpha)E^{0.92}_\alpha} \right) - 0.312 - \frac{1.098E_\alpha}{RT} \tag{3}
\]

In these equations, T was temperature (K), \( \beta \) was heating rate (K/min), A was pre-exponential factor (min\(^{-1}\)), R was ideal gas constant (8.314 J/mol K), \( E_a \) is activation energy (kJ/mol), \( \alpha \) is conversion factor and \( g(\alpha) \) is function of conversion factor. Based on the equation, A and \( E_a \) were calculated using the intercept and slope values, respectively.

3. Results and discussion

Dynamic thermogravimetric analysis was executed to evaluate the decomposition temperatures of DABCO-based ILs with various anions, namely [DABCODBS][HSO\(_4\)], [DABCODBS][CF\(_3\)SO\(_3\)] and [DABCODBS][Cl\(_2\)] ILs. Figure 2 illustrates the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of all three ILs with different anions for various heating rates which are 10, 15, 20 and 25 °C/min, respectively. Both TG and DTG curves for each IL show constant pattern behavior. This is accredited to similar reaction mechanism for each individual IL regardless of heating rate [26]. The shifting of curve towards right side has shown the increase of thermal decomposition. The increment trending of thermal decomposition with increasing heating rate as thermodynamics and decomposition kinetics influenced the thermal decomposition rate [27].

The thermal decomposition of ILs is usually represented by the onset temperature of the TG curve. The onset temperature can be extracted from the TG curve by the intersection of the mass at 100% with the tangent of the curve. Based on Figure 2, the comparison of the first onset temperature of TG curve for all three ILs shows a decreasing temperature (onset) trend in sequence of [DABCODBS] [Cl\(_2\)] > [DABCODBS][HSO\(_4\)] > [DABCODBS][CF\(_3\)SO\(_3\)] with the onset temperature range of 351.4-366.2°C, 155.1-166.1°C and 140.1-151.8°C, respectively. Even though ILs with halide anions are known to have low thermal stability due to their higher basicity [28], in this case, IL with Cl\(_2\) anion has highest onset temperature. The high thermal stability of ILs with Cl\(_2\) anion can be due to less steric hindrance of ILs as the anion is less bulky compare to the other two ILs [29]. Besides that, additional sulfonyl group in HSO\(_4\) and CF\(_3\)SO\(_3\) anions also lower the thermal stability of the ILs [30].

In general, the ILs may decomposed by defragmentation to a range of volatile degradation product of simply revert back to starting materials [31,32]. The decomposition mechanisms are highly dependent on the structure of ILs. In TG and DTG curves of all three ILs, [DABCODBS][Cl\(_2\)] curves depict that one-step decomposition mechanism is taking place while [DABCODBS][HSO\(_4\)] and [DABCODBS][CF\(_3\)SO\(_3\)] curves show more than one step decomposition mechanism is involved. The small mass loss at low temperature of the first onset temperature for [DABCODBS][HSO\(_4\)] and [DABCODBS][CF\(_3\)SO\(_3\)] TG curves can be accredited to the evaporation and decomposition of the ILs. The multi-step decomposition mechanism also may be due to separate decomposition of cation.
and anion. Liang et al (2013) has also determined multi-step decomposition reaction for their cyano-functionalized imidazolium-based ILs which has HSO₄⁻ anion [33].

Figure 2. TG and DTG curves of (a) [[DABCODBS][HSO₄]₂], (b) [[DABCODBS][CF₃SO₃]₂] and (c) [[DABCODBS][Cl]₂] at various heating rate.

The thermal decomposition kinetic parameters for ILs, namely, activation energy, $E_a$ and pre-exponential factor, $A$ can be calculated through DTG and TG approaches. Through DTG approach, the value of $T_{max}$ which is the peak temperature in DTG curve is extracted and used in the mathematical model for thermokinetic study. However, this approach is only suitable for one-step thermal decomposition mechanism [34]. Therefore, in this study, TG approach is used instead. In TG approach, the kinetic parameters are calculated distinctively for each fraction conversion, $\alpha$. The trend for kinetic parameters is then compared to define number of step for thermal decomposition mechanism. In order to compare the kinetic parameters for thermal decomposition of various ILs, the average value is calculated. For this research, KAS, FWO and Starink methods are used to calculate the kinetic parameters using equation (1), (2) and (3), respectively as mentioned in experimental section. From the equations, kinetic parameters are derived as equation (4) and (5) for KAS method, equation (6) and (7) for FWO method and equation (8) and (9) for Starink method:
Figure 3, 4 and 5 depict the thermokinetics plot of KAS, FWO and Starink methods and activation energy, \( E_a \) at various conversion, \( \alpha \) for [DABCODBS][HSO\(_4\)]\(_2\), [DABCODBS][CF\(_3\)SO\(_3\)]\(_2\) and [DABCODBS][Cl]\(_2\) ILs, respectively. The results presented through all kinetic methods for all ILs are in close agreement with each other. For [DABCODBS][HSO\(_4\)]\(_2\) and [DABCODBS][CF\(_3\)SO\(_3\)]\(_2\) ILs activation energy, \( E_a \) plot in Figure 3d and 4d, respectively, there are slight increase of \( E_a \) at lower conversion degree, \( \alpha \). This results may be due to evaporation or partial thermal decomposition of ILs at lower temperature. After that, the \( E_a \) trending fluctuate showing the multi-step thermal decomposition mechanism of ILs where intermediates are formed during decomposition process due to complexity of IL structure [35]. For [DABCODBS][Cl]\(_2\) IL activation energy, \( E_a \) plot in Figure 5d, the \( E_a \) trending is almost constant at \( \alpha > 0.1 \). This result is attributed to a one-step thermal decomposition mechanism of IL where no intermediate is formed during the decomposition process.

The average kinetic parameters are then calculated at conversion degree, \( \alpha = 0.3 – 0.7 \) as suggested by literatures [36,37] and the values are listed in Table 1. The average activation energy (\( E_a \)) calculated by KAS, FWO and Starink methods for [DABCODBS][HSO\(_4\)]\(_2\) are 163.49 kJ/mol, 173.33 kJ/mol and 162.58 kJ/mol. For [DABCODBS][CF\(_3\)SO\(_3\)]\(_2\), the \( E_a \) values are 119.59 kJ/mol, 130.41 kJ/mol and 119.07 kJ/mol respectively. For [DABCODBS][Cl]\(_2\) the \( E_a \) values are 199.72 kJ/mol, 210.50 kJ/mol and 198.63 kJ/mol. While pre-exponential factor, presented in term of Log \( A \) calculated by KAS, FWO and Starink methods are 13.96 min\(^{-1}\), 14.13 min\(^{-1}\) and 14.33 min\(^{-1}\) for [DABCODBS][HSO\(_4\)]\(_2\), 8.96 min\(^{-1}\), 9.42 min\(^{-1}\) and 9.34 min\(^{-1}\) for [DABCODBS][CF\(_3\)SO\(_3\)]\(_2\), and 15.85 min\(^{-1}\), 15.87 min\(^{-1}\) and 16.21 min\(^{-1}\) for [DABCODBS][Cl]\(_2\), respectively. All the values calculated using the three methods show good correlation. The highest activation energy for thermal
decomposition was found for [DABCODBS][Cl]2 and the lowest was [DABCODBS][CF3SO3]2. It can be deduced from the results, the decreasing thermal stability trend of [DABCODBS][Cl]2> [DABCODBS][HSO4]2 > [DABCODBS][CF3SO3]2.

![Figure 4. Thermokinetics of ([DABCODBS][CF3SO3]2) using KAS (a), FWO (b) and Starink (c) method, and also the activation energy profiles (d).](image)

![Figure 5. Thermokinetics of ([DABCODBS][Cl]2) using KAS (a), FWO (b) and Starink (c) method, and also the activation energy profiles (d).](image)

**Table 1.** Average activation energy, $E_a$ and pre-exponential factor in term of Log A for ILs using KAS, FWO and Starink methods

| Method            | KAS   | FWO   | Starink |
|-------------------|-------|-------|---------|
| Kinetic parameters| $E_a$ (kJ/mol) | $\log A$ (min$^{-1}$) | $E_a$ (kJ/mol) | $\log A$ (min$^{-1}$) | $E_a$ (kJ/mol) | $\log A$ (min$^{-1}$) |
| [DABCODBS][HSO4]2 | 163.49 | 13.96 | 173.33 | 14.13 | 162.58 | 14.33 |
| [DABCODBS][CF3SO3]2 | 119.59 | 8.96 | 130.41 | 9.42 | 119.07 | 9.34 |
| [DABCODBS][Cl]2 | 199.72 | 15.85 | 210.50 | 15.87 | 198.63 | 16.21 |

4. Conclusion

Thermokinetic study of DABCO-based IL with three types of anions, namely [DABCODBS][HSO4]2, [DABCODBS][CF3SO3]2 and [DABCODBS][Cl]2. ILs has been executed using TG approach following KAS, FWO and Starink method. The results determined from all the three methods are in
close agreement with each other. The ILs are thermally stable before reaching an onset temperature range of 155.1-166.1 °C for [DABCODBS][HSO₄]₂ IL, 140.1-151.8 °C for [DABCODBS][CF₃SO₂] IL and 351.4-366.2 °C for [DABCODBS][Cl]₂ IL. The average kinetic parameters (Eₗ and Log A) are calculated for KAS, FWO and Starink methods. The results also have shown a decreasing thermal stability trend of [DABCODBS][Cl]₂ > [DABCODBS][HSO₄]₂ > [DABCODBS][CF₃SO₂]₂. Intermediates are formed for [DABCODBS][CF₃SO₂]₂ and [DABCODBS][HSO₄]₂ until achieved total decomposition, while there is no intermediate formed for the pyrolysis kinetic of [DABCODBS][Cl]₂.

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