

Research Article

Open Access

Thermal Characteristics of 1-Butyl-3-Methylimidazolium Based Oxidant Ionic Liquids

Jaganathan JR¹, Sivapragasam M¹ and Wilfred CD^{1,2*}

¹Centre for Research on Ionic Liquids (CORIL), University of Technology Petronas, Bandar Seri Iskandar, 32610, Perak, Malaysia

²Fundamental and Applied Sciences Department, University of Technology Petronas, Bandar Seri Iskandar, 32610, Perak, Malaysia

Abstract

This study investigates the thermal properties of a series of 1-butyl-3-methylimidazolium based ionic liquids (ILs) possessing various oxidative anions such as dichromate ($\text{Cr}_2\text{O}_7^{2-}$), nitrate (NO_3^-), hydrogen sulphate (HSO_4^-), tetrafluoroborate (BF_4^-), perchlorate (ClO_4^-) and hexafluorophosphate (PF_6^-). The synthesized ILs were defined by their thermal properties in terms of glass transitions, melting and decomposition temperatures. The effect of oxidant anions on activation energy of ILs were computed by non-isothermal kinetic methods i.e., through were of Ozawa and Kissinger's methods. The most thermally stable IL was seen to be the transition metal-containing IL [bmim] $\text{Cr}_2\text{O}_7^{2-}$ where it recorded the highest activation energy of 11.65 kJ/mole using Ozawa method and 15.71 kJ/mole using Kissinger method compared to other ILs. The lowest activation energy was obtained for [bmim] BF_4^- and [bmim] PF_6^- . Based on the detailed thermal behavior of this high temperature oxidant ILs, it can potentially be beneficial for desulfurization applications.

Keywords: Activation energy; DSC; Kinetics; Oxidant ionic liquids; TGA

Introduction

Ionic Liquids (ILs), best described as “designer solvents”, have been known to be easily tunable by a selection of ionic species so as to own a plethora of chemical and physical functionalities. By combining an oxidative anion with an organic cation such imidazolium (Figure 1), oxidative ILs can be tuned to be of function in separation and extraction [1], catalysis [2,3] electrochemistry [4], analytics [5] and as solvents for many different processes [6,7]. For example, various anions like hydrogen sulphate (HSO_4^-), tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) paired with 1-butyl-3-imidazolium (bmim) cations are widely used for oxidation of aromatic aldehydes [8] and oxidative desulfurization [9]. Pyridinium dichromate [10] and quinolinium dichromate [11] based ILs have been also used as an oxidant in the oxidation of aldehydes. Past decades have seen a combination of oxidative desulfurization with imidazolium based ILs drawing a lot of attention [12-15]. Conventionally, ILs was used as an extractant; acetic acid as a catalyst and H_2O_2 as the oxidant. However, high

concentrations of H_2O_2 , is potentially explosive [15,16]. This common method of desulfurization is widely used but less robust in treating benzothiophenes and dibenzothiophenes; nonetheless imidazolium based ILs, are said to possess very good extractive properties on these sulfur containing compounds [17]. In achieving deep desulfurization, stringent conditions such as high temperatures, high pressure and high hydrogen consumption are required [16]. Hence, knowledge on the stability of ILs at high temperatures is a vital factor in preventing early degradation so as to eliminate existing discrepancies. Thermal stability of ILs depends primarily on the anion, with the effect of the cation being less significant [18]. In this study we focus on analyzing the thermal behavior of a series of bmim based ILs with various oxidant anions such as $\text{Cr}_2\text{O}_7^{2-}$, ClO_4^- , NO_3^- (strongly coordinating anions); and HSO_4^- , BF_4^- , PF_6^- (weakly coordinating anions). The effect of various oxidant anions on the activation energy (E_a) of ILs was studied by applying the Ozawa and Kissinger non-isothermal kinetic method. This is *in lieu* with the recommendations by the ICTAT Kinetics Committee (2011) [19] and Starink [20] that mention these kinetic methods to be one of the best iso-conversion methods available to compute activation energy based on accuracy and reliability of the results. The Kissinger method was also said to offer a significant improvement in the accuracy of the activation energy values compared to the Ozawa method. Calculating E_a is important to have a better understanding on the kinetic behavior and thermal sensitivity of any material. The minimum energy required to decompose a material at various stages can be obtained from the E_a . Cao and Mu [21] comprehensively reported the thermal analysis of 66

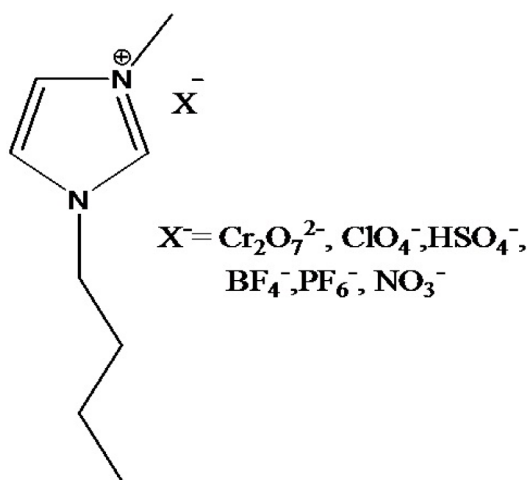


Figure 1: Structure of [Bmim] with various oxidant anions.

***Corresponding author:** Wilfred CD, Centre for Research on Ionic Liquids (CORIL), Fundamental and Applied Sciences Department, University of Technology Petronas, Bandar Seri Iskandar, 32610, Perak, Malaysia, Tel: 6053687635; Fax: 6053656176; E-mail: cecil@petronas.com.my

Received October 18, 2016; **Accepted** October 21, 2016; **Published** October 28, 2016

Citation: Jaganathan JR, Sivapragasam M, Wilfred CD (2016) Thermal Characteristics of 1-Butyl-3-Methylimidazolium Based Oxidant Ionic Liquids. J Chem Eng Process Technol 7: 309. doi: 10.4172/2157-7048.1000309

Copyright: © 2016 Jaganathan JR, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

ILs (comprising of 19 cations and 20 anions) using the pseudo-zero order rate expression to obtain E_a values with five different levels of onset decomposition temperatures. However, no data was reported on E_a using Ozawa and Kissinger methods. Another study by Ferreira et al. [22] also lacked information on aforesaid parameters but they obtained thermal stability of ILs using a polynomial function which is associated with heat capacity. Studies by Navarro et al. [23], emphasized on calculating E_a of binary ILs *via* first order model by applying Arrhenius's Law. This work then aims to fill the gap of finding E_a of oxidant ILs based on the two models proposed; to which our knowledge has not been reported elsewhere.

Material and Methods

Materials

The following chemicals have been used in this experiment; 1-methyl-3-butyl-imidazolium chloride (Merck, >98%), 1-methyl-3-butyl-imidazoliumbromide (Merck, >98%), Sodium tetrafluoroborate (Fluka, >98%), sodium hexafluorophosphate (Fischer, >98%), sodium hydrogen sulphate (Merck), Chromium trioxide (Sigma, >99%), sodium perchlorate (Sigma, >98%), silver nitrate (Merck Millipore), dichloromethane (Merck Millipore), decolorizing charcoal and acetonitrile (Merck Millipore). All of these chemicals were used as obtained without further purification.

Methods

Synthesis of ILs

1-methyl-3-butyl-imidazolium tetrafluoroborate, [bmim]BF₄ was synthesized as per literature procedure [24]. The [bmim]Br (10.95 g, 0.05 mol) was dissolved in 100 mL of water in a double necked round bottom flask. NaBF₄ (5.49 g, 0.05 mol) was added to the mixture and the final mixture was stirred for 24 hrs at room temperature. The resultant mixture was extracted with DCM to filter out bromide salt. Due to the hydrophilicity of [bmim]BF₄, the IL was dissolved in water phase leaving white sodium bromide precipitate in DCM which was filtered out. This process was repeated twice to ensure the complete removal of bromide salt. This was confirmed using silver nitrate titration. Organic solvents were then removed on a rotary evaporator under reduced pressure and [bmim]BF₄ were obtained in good yield (72%). Other remaining ILs, [bmim]PF₆ (70% yield), [bmim]HSO₄ (68% yield), [bmim]Cr₂O₇ (55% yield), [bmim]ClO₄ (72% yield) and [bmim]NO₃ (65% yield), were synthesized *via* similar metathesis reaction [25-29].

Characterization

Proton nuclei was measured by Nuclear Magnetic Resonance (¹H NMR spectrometer Bruker Avance II Plus 500 MHz). ¹H NMR spectrum for [bmim] HSO₄⁻ is exhibited as (500 MHz, [D₆]Acetone): δ: 8.98 (s, 1 H), 7.75 (d, 1 H), 7.70 (d, 1 H), 4.34 (t, 2H), 4.06 (s, 3H), 1.92 (q, 2H), 1.39 (m, 2H), 0.94 (t, 3H). ¹³C NMR (500 MHz, [D₆] Acetone): δ: 135.76, 123.37, 122.11, 49.17, 35.51, 31.17, 18.61, 12.52. Fourier Transform Infrared Spectroscopy was performed on Perkin-Elmer 6700 FT-IR in the range of 4000-400 cm⁻¹. Water content was determined by Karl Fischer Coulometer, (Mettler Toledo) and was maintained under 1000 ppm. Thermal analysis was carried out by thermogravimetry analysis (TGA, Perkin-Elmer STA 6000) and Differential scanning calorimetry (DSC, Mettler Toledo).

FT-IR Identification of ILs

Characteristic peaks for all synthesized ILs are displayed in Table 1. FT-IR spectrograph of bmim[HSO₄] is displayed in Figure 2.

Results and Discussion

Glass Transition (T_g)

Melting point (T_m) and glass transition temperature (T_g) of ILs were determined by differential scanning calorimetry (DSC, Mettler Toledo), heating range from -150°C to 130°C. Highest T_g value was observed for [bmim]Cr₂O₇ which is 14.5°C and the lowest for [bmim] BF₄ (Table 2) Melting endothermic peaks were only observed for [bmim]PF₆ and [bmim]NO₃.

Decomposition of ILs

Samples were heated from 50°C-800°C at 10°C/min under N₂ atmosphere. (T_{onset}) which represents the first temperature where any measurable weight loss was observed (Figure 3). Generally, most ILs exhibited high decomposition temperatures ranging from (300-400°C). It can be clearly observed from Figure 3 that [bmim]Cr₂O₇ is thermally stable even up to 800°C with 73% weight loss despite a low initial degradation step. This goes to show that the cation has little effect on decomposition temperature. In an investigation by Cao and Mu [21], it was concluded that the metal coordinating nature on the anion has the effect to lower thermal degradation points. Crosthwaith et al. [34] stated that the decomposition temperature primarily depended on the coordinating nature of the anions in the ILs. We are also able to deduce that the decomposition temperature (T_{comp}) is much lower for highly coordinating anions, as observed in Table 2. The ILs, [bmim]Cr₂O₇ and [bmim]NO₃ had the lowest degradation temperature which is due to the strongly coordinating anions compared to weakly coordinating anion species like BF₄⁻, PF₆⁻, ClO₄⁻ and HSO₄⁻. This is congenial with results from Crosthwaith et al. [34] where decomposition temperature for poorly coordinating anions such as bis(trifluoromethylsulfonyl)imide

ILs	Characteristics			
	Cation	Ref	Anion	Ref
[Bmim]PF ₆ [Bmim]BF ₄ [Bmim]HSO ₄ [Bmim]ClO ₄ [Bmim]NO ₃ [Bmim]Cr ₂ O ₇	3158 and 3119 (C-H stretching from imidazole ring), 2964 and 2938 C-H,CH ₂ and CH ₃ stretching peak on lateral chain of imidazole ring, 1574 and 1467 (skeletal vibration peaks of imidazole ring) 1170 (in-plane bending vibration peak of C-H from imidazole ring)	[22]	832, 1015, 1033 and 1045 for B-F stretching vibration 1305(S=O stretching), 1198 (antisymmetric SO ₂ stretching) and 1164 (SOH bending modes) 1088, 1347 (antisymmetric NO stretching) 930, 875, 765 and 730	[12,24-27]

Table 1: Table showing characteristics of Ionic liquids.

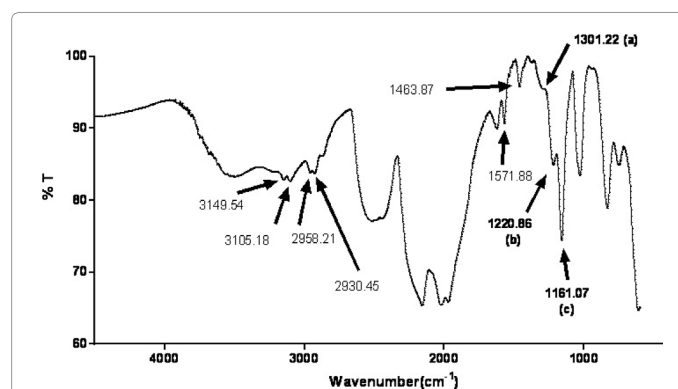


Figure 2: Fourier Transform Infra-Red (FTIR) spectra for [Bmim]HSO₄. (a) S=O stretching (b) antisymmetric SO₂ stretching (c) SOH bending.

ILs	Glass Transition (DSC) (T_g)/°C	T_g /°C (lit)	Melting (DSC) T_m /°C	T_m /°C (lit)	Onset Degradation from TGA (T_{onset})/°C	T_{onset} /°C (lit)	Charred Residue at 800°C
[Bmim]PF ₆	-76	[30]	-8	[30]	402.26	[15,30]	0.95
[Bmim]BF ₄	-85	[30]	-	[30]	372.73	[15,30]	0.55
[Bmim]HSO ₄	-58		-		342.14	[15]	0.48
[Bmim]ClO ₄	-17		-		320.09	[15,22]	0.83
[Bmim]NO ₃	-		17.7		297.49	[15]	0.38
[Bmim]Cr ₂ O ₇	14.5		-		239.34	[15]	27.49

Table 2: Table showing characteristics of Ionic liquids along with T_g , T_m and T_{onset} .

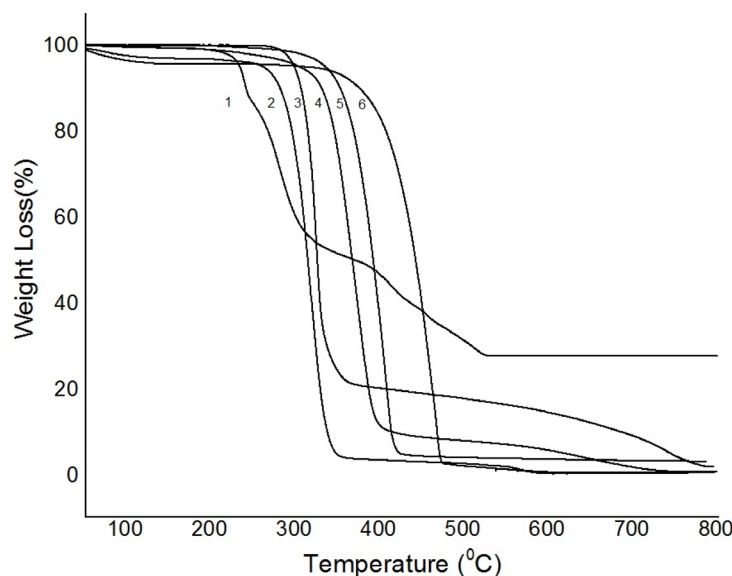


Figure 3: Thermogravimetric analysis of ILs at 10°C/min (1) [Bmim]Cr₂O₇, (2) [Bmim]NO₃, (3) [Bmim]ClO₄, (4) [Bmim]HSO₄, (5) [Bmim]BF₄, (6) [Bmim]PF₆.

[Tf₂N] and tetrafluoroborate [BF₄]⁻ were low. In a series of pyridinium and imidazolium based ILs, it was found that the nature of cation had a small effect on the decomposition temperature (T_{comp}). On the other hand, the formation of thermally stable metal oxide by [bmim] Cr₂O₇ may account to greater stability which produced 27.49% charred residue at 800°C. The degradation temperature of the remaining ILs which had weak coordinating anions increased in the order of [bmim]ClO₄ < [bmim]HSO₄ < [bmim]BF₄ < [bmim]PF₆. The effect of anion on density is relatively obvious and it increases with an increase in size of anion [28]. 'Inter molecular' attraction also contributed to high degradation temperatures. For example, the PF₆⁻ anion has an octahedral shape which is more symmetrical compared to the tetrahedral ClO₄⁻ anion, thus making the *van der Waals* attractive forces stronger between PF₆⁻ compared to ClO₄⁻ anion. This correlates with a high density value (Table 3) obtained for [bmim]PF₆ (1.33 g/cm³) compared to that of [bmim]ClO₄ (1.26 g/cm³). Halogen containing anions such as [BF₄]⁻ and [PF₆]⁻ are unstable and tend to decompose to hydrogen fluoride (HF) in the presence of water and disrupts the purity of ILs. Another relaying factor affecting thermal stability of ILs is the nucleophilicity and the hydrophobicity of the corresponding anions [35]. The effect of various heating rates for [bmim]NO₃ is shown in Figure 4. At high heating rates, the degradation peak shifted to a higher temperature for all cases and ILs were thermally stable at a high heating rate. Data extracted from Figure 4 are the vital factors in computing degradation kinetics of ILs in the next section.

Degradation kinetics of ILs

The Ozawa and Kissinger method were applied to quantify the value of E_a despite various available methods for the evaluation of the

non-isothermal kinetic parameters. An advantage of these methods is that it does not require knowledge of the reaction mechanism and has reliable accuracy of E_a [13].

Arrhenius equation generally can be written as follows;

$$K = K_0 \exp^{-E_a/RT} \quad (1)$$

Where E_a is the activation energy for decomposition, K_0 is the pre-exponential factor and R is the gas constant. The non-isothermal decomposition is characterized by a constant heating rate. The relationship between the sample temperature T and the heating rate can be written as;

$$T = T_0 + \dot{\alpha}t \quad (2)$$

Kissinger and Ozawa equations can be written with the highest rate of decomposition at maximum peak approximations, respectively;

$$\ln\left(\frac{\beta}{T^2}\right) = \frac{-E_a}{RT_p} + \ln\left(\frac{K_0 E_a}{R}\right) \quad (3)$$

$$\ln \beta = \frac{-E_a}{RT_p} + \ln\left(\frac{K_0 E_a}{R}\right) \quad (4)$$

T_p is maximum decomposition temperature, β ; heating rate, B values were obtained by TGA at several heating rates. Heating rates of 10°C/min, 15°C/min, 20°C/min and 25°C/min were used in this study.

The value of E_a can be computed by Ozawa and Kissinger's method for any particular degree of decomposition which can be determined

from the linear dependence of $\ln \beta$ versus $1/T_p$ (Figure 5 - Ozawa) and $\ln(\beta/T^2)$ versus $1/T_p$ (Figure 6 - Kissinger) at different heating rates without knowledge of the reaction order. E value can be directly obtained at a fixed conversion with the slope being $-E_a/R$. Based on results in Table 4, it can be said that the E_a obtained by Kissinger method recorded slightly higher results than the Ozawa method, but remained in a comparable range. [bmim] BF_4 and [bmim] PF_6 had similar yet lowest E_a values compared to other ILs. Increasing trend in E_a was also observed upon switching from fluorinated to oxygenated anion. This could be explained by the formation of oxides by the anion at various stages which acted as a thermal barrier providing a complicated pathway for breakdown to take place during the heating process. This in turn

resulted in an increase in the decomposition temperature. However, the E_a for [bmim] Cr_2O_7 is the highest compared to all other oxidant despite exhibiting low degradation temperature. Such complexed thermal profile is most likely due to the presence of more than one crystallographic structures of dichromate ion as discussed by [27] and the formation of metal oxides which led to greater thermal resistance.

Conclusion

Thermal characteristics of 1-butyl-3-methylimidazolium based oxidant ILs were studied by TGA and DSC. Non-isothermal kinetic technique by Ozawa and Kissinger's was applied to determine the change in E_a for various oxidant anions. E_a for ILs with fluorinated

ILs	Linear Correlation Factor (R^2)	Average E_a by Ozawa (kJ/mole)	Linear Correlation Factor (R^2)	Average E_a by Kissinger (kJ/mole)
Bmim Cr_2O_7	0.958	11.65	0.966	15.71
Bmim HSO_4	0.994	7.92	0.954	8.90
Bmim ClO_4	0.951	7.55	0.984	8.52
Bmim NO_3	0.999	5.53	0.984	4.15
Bmim BF_4	0.989	3.02	0.937	4.72
Bmim PF_6	0.996	3.03	0.991	5.35

Table 3: Table showing linear correlation factors of Ionic liquids.

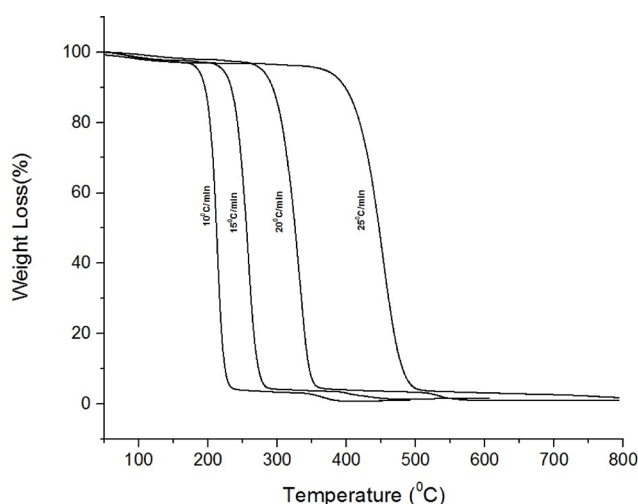


Figure 4: Thermogravimetric analysis of [Bmim] NO_3 at various heating rates.

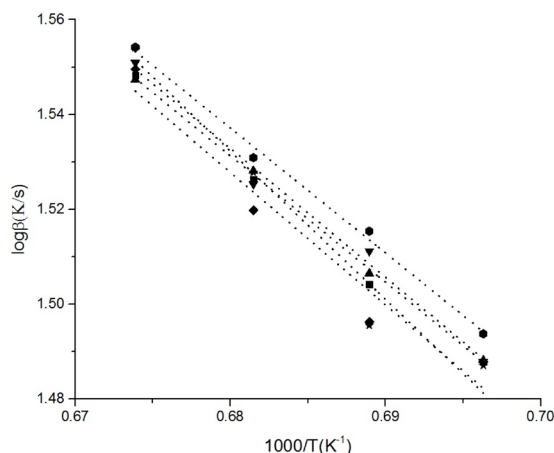
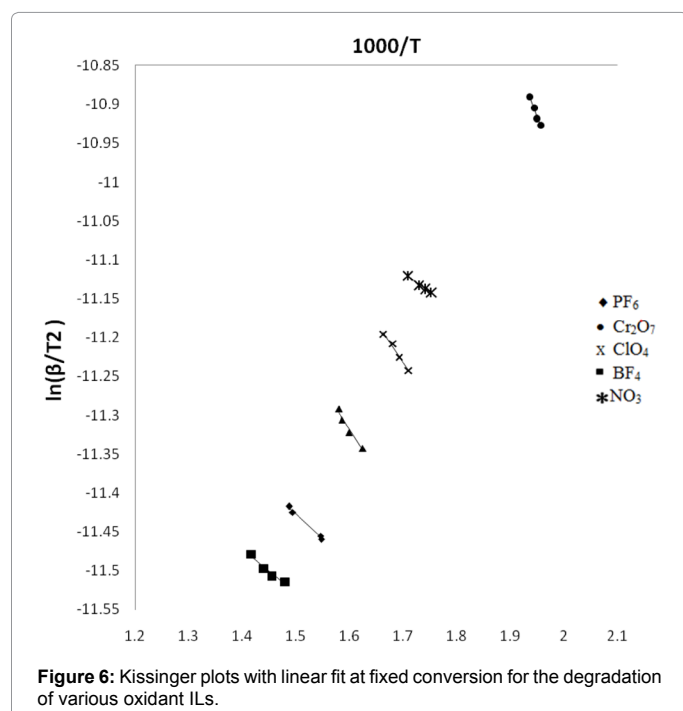


Figure 5: Ozawa plots with linear fit at fixed conversion for the degradation of various oxidant ILs: ■ [Bmim][PF_6]; ▼ [Bmim][BF_4]; ▲ [Bmim][NO_3]; ♦ [Bmim][ClO_4]; ● [Bmim][HSO_4]; ★ [Bmim][BF_4].



ILs	Appearance	Density (g/cm ³)
Bmim Cr ₂ O ₇	Dark brown	1.43
Bmim HSO ₄	Mild Brown	1.28
Bmim ClO ₄	Dark Brown	1.26
Bmim NO ₃	Mild Brown	1.39
Bmim BF ₄	Light Brown	1.31
Bmim PF ₆	Brown	1.33

Table 4: Table showing Appearance and Densities of Ionic liquids.

anion were found to be lower than the oxygenated containing anions. Increasing trend in E_a and decomposition temperatures were observed as the oxygen atoms in the anion increases. The density due to molar mass of anion was also believed to contribute to greater thermal stability of ILs.

Acknowledgements

The present work has been supported by the Centre of Research in Ionic Liquids (CORIL), Universiti Teknologi, Petronas, Malaysia.

References

- Han D, Row KH (2010) Recent applications of ionic liquids in separation technology. *Molecules* 15: 2405-2426.
- Olivier-Bourbigou H, Magna L, Morvan D (2010) Ionic liquids and catalysis: recent progress from knowledge to applications. *Appl Catal A Gen* 373: 1-56.
- Bogel-Lukasik E, Santos S, Bogel-Lukasik R, da Ponte MN (2010) Selectivity enhancement in the catalytic heterogeneous hydrogenation of limonene in supercritical carbon dioxide by an ionic liquid. *J Supercrit Fluids* 54: 210-217.
- Shiddiky MJ, Torriero AA (2011) Application of ionic liquids in electrochemical sensing systems. *Biosens Bioelectron* 26: 1775-1787.
- Sun P, Armstrong DW (2010) Ionic liquids in analytical chemistry. *Anal Chim Acta* 661: 1-16.
- Earle MJ, Seddon KR (2000) Ionic liquids. Green solvents for the future. *Pure Appl Chem* 772: 1391-1398.
- Rogers RD, Seddon KR (2003) Chemistry. Ionic liquids--solvents of the future? *Science* 302: 792-793.
- Howarth J (2000) Oxidation of aromatic aldehydes in the ionic liquid [bmim] PF₆. *Tetrahedron Lett* 41: 6627-6629.
- Gao H, Guo C, Xing J, Zhao J, Liu H (2010) Extraction and oxidative desulfurization of diesel fuel catalyzed by a Brønsted acidic ionic liquid at room temperature. *Green Chem* 12: 1220-1224.
- Corey EJ, Schmidt G (1979) Useful procedures for the oxidation of alcohols involving pyridinium dichromate in aprotic media. *Tetrahedron Lett* 5: 399-402.
- Chaubey GS, Kharsyntiew B, Mahanti MK (2004) Oxidation of substituted 2-furaldehydes by quinolinium dichromate: a kinetic study. *J Phys Org Chem* 17: 83-87.
- Cai YQ, Song GH, Liang DN (2015) Desulfurization using the 1,2-dimethylimidazolium ionic liquid as an adsorbent. *Chinese Chemical Lett* 26: 317-319.
- Dharaskar SA, Wasewar KL, Varma MN, Shende DZ (2010) Imidazolium ionic liquid as energy efficient solvent for desulfurization of liquid fuel. *Sep Purif Technol* 155: 101-109.
- Rodríguez-Cabo B, Rodríguez H, Rodil E, Arce A, Soto A (2014) Extractive and oxidative- extractive desulfurization of fuels with ionic liquids. *Fuel* 117: 882-889.
- Nie Y, Dong Y, Bai L, Dong H, Zhang X (2013) Fast oxidative desulfurization of fuel oil using dialkylpyridiniumtetrachloroferrates ionic liquids. *Fuel* 103: 997-1002.
- Jiang W, Zhu W, Chang Y, Li H, Chao Y, et al. (2014) Oxidation of Aromatic Sulfur Compounds Catalyzed by Organic Hexacyanoferrates in Ionic Liquids with a Low Concentration of H₂O₂ as an Oxidant. *Energy Fuels* 28: 2754-2760.
- Chen X, Song D, Asumana C, Yu G (2012) Deep oxidative desulfurization of diesel fuels by Lewis acidic ionic liquids based on 1-n-butyl-3-methylimidazolium metal chloride. *J Mol Catal A-Chem* 359: 8-13.
- Salgado J, Parajó JJ, Fernández J, Villanueva M (2014) Long-term thermal stability of some 1-butyl-1-methylpyrrolidinium ionic liquids. *J Chem Thermodyn* 74: 51-57.
- Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C (2011) ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim Acta* 520: 1-19.
- Starink MJ (2003) The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. *Thermochim Acta* 404: 163-176.
- Cao Y, Mu T (2014) Comprehensive Investigation on the Thermal Stability of 66 Ionic Liquids by Thermogravimetric Analysis. *Ind Eng Chem Res* 53: 8651-8664.
- Ferreira AF, Simoes PN, Ferreira AGM (2012) Quaternary phosphonium-based ionic liquids: Thermal stability and heat capacity of the liquid phase. *J Chem Thermodyn* 45: 16-27.
- Navarro P, Larriba M, García J, Rodríguez F (2014) Thermal stability and specific heats of {[emim][DCA] + [emim][TCM]} mixed ionic liquids. *Thermochim Acta* 588: 22-27.
- Baker SN, Brauns EB, McCleskey TM, Burrell AK, Baker, GA (2006) Fluorescence Quenching Immunoassay Performed in an Ionic Liquid. *Chem Commun* 27: 2851-2853.
- Carda-Broch S, Berthod A, Armstrong DW (2003) Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. *Anal Bioanal Chem* 375: 191-199.
- Zhang W, Xu K, Zhang Q, Liu D, Wu S, et al. (2014) Oxidative Desulfurization of Dibenzothiophene Catalyzed by Ionic Liquid [Bmim]HSO₄. *Ind Eng Chem Res* 49: 11760-11763.
- Fosse N, Joubert O, Ganne M, Brohan L (2001) Tetramethylammonium dichromate and trichromate. *Solid State Sci* 3: 121-132.
- Dan WX, Yuan WW, Feng TUG, Xi JK (2010) Synthesis and physico-chemical properties of new green electrolyte 1-butyl-3-methylimidazolium perchlorate. *Trans Nonferrous Met Soc China* 20: 2032-2036.
- Robin DR, Kenneth RS, Sergei V (2003) Green Industrial Applications of Ionic Liquids. Vol 92, Springer, Cold Harbour, NY, USA.
- Jung OS, Kim YJ, Lee YA, Park KM, Lee SS (2003) Subtle Role of Polyatomic Anions in Molecular Construction: Structures and Properties of AgX Bearing

- 2,4-Thiobis(pyridine) (X-) NO₃-, BF₄-, ClO₄-, PF₆-, CF₃CO₂-, and CF₃SO₃-. Inorg Chem 42: 844-850.
31. Holomb R, Martinelli A, Albinsson I, Lassegue JC, Johansson P, et al. (2008) Ionic liquid structure: the conformational isomerism in 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]). J Raman Spectrosc 39: 793-805.
32. Yacovitch TI, Wende T, Jiang L, Heine N, Meijer G, et al. (2011) Infrared Spectroscopy of Hydrated Bisulfate Anion Clusters: HSO₄⁻·h(H₂O)₁₋₁₆. J Phys Chem Lett 2: 2135-2140.
33. Hebert GN, Odom MA, Bowman SC, Strauss SH (2004) Attenuated total reflectance FTIR detection and quantification of low concentrations of aqueous polyatomic anions. Anal Chem 76: 781-787.
34. Crosthwaite JM, Muldoon MJ, Dixon JK, Anderson JL, Brennecke JF (2005) Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. J Chem Thermodyn 37: 559-568.
35. Pinkert A, Marsh KN, Pang S, Staiger MP (2009) Ionic liquids and their interaction with cellulose. Chem Rev 109: 6712-6728.
36. Fredlake CP, Crosthwaite JM, Hert DG, Aki SNVK, Brennecke JF (2004) Thermophysical Properties of Imidazolium-Based Ionic Liquids. J Chem Eng Data 49: 954-964.