Thermophysical Properties of 1-Ethyl-3-methylimidazolium Ethylsulfate and 1-Butyl-3-methylimidazolium Methylsulfate Ionic Liquids

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Heat capacity, glass-transition, crystallization, and melting temperatures of 1-ethyl-3-methylimidazolium ethylsulfate ([Emim][$EtSO_4$]) and 1-butyl-3-methylimidazolium methylsulfate ([Bmim][$MeSO_4$]) ionic liquids (ILs) have been determined by differential scanning calorimetry (DSC). Their thermal stabilities have been analyzed by thermogravimetric analysis (TGA). Given the effect of the heating rate over the decomposition temperatures, isothermal TGA experiments are proposed as a more appropriate method to evaluate the thermal stability of the ILs. Inside the working range (−150 °C to 30 °C), [Emim][$EtSO_4$] and [Bmim][$MeSO_4$] present a glass-transition temperature of −78.4 °C and −91.9 °C, respectively. [Bmim][$MeSO_4$] has a melting temperature of −4.1 °C. The C_p was determined in a working range (10 °C to 100 °C) where its value increases lineally with temperature.

Introduction

Ionic liquids (ILs) are considered as solvent in reactions or chemical separations in a variety of applications.[1,2] The growing interest in the use of ILs in the power sector is well-known, specifically in the field of renewable energy[3] as electrolytes for solar cells,[4] fuel cells,[5] or heat transfer fluid.[6] Given that this and other similar applications require operations at high temperatures, the thermal stability of the ILs must be understood and evaluated.

Basically, the thermal stability of an IL depends on the anion, and the effect of the cation on the stability is rather insignificant.[7] Thermal stability increases with the anion size and decreases with its hydrophilicity.[2,8] It can be evaluated by thermal property measurements. The stability study based on the measurement of thermal events (melting point, decomposition, glass transition temperature, heat capacity, etc.) consists of taking characteristic temperatures of ILs in isothermal and/or nonisothermal conditions as a function of time.[9] These thermal events could be measured by cold stage polarizing microscopy, thermogravimetric analyses (TGA), and differential scanning calorimetry (DSC) techniques.[10] Extensively, the heat capacity, glass-transition, freezing, and melting temperatures can be taken by DSC, and the decomposition temperatures of ILs can be obtained by TGA.[2,11,12]

In this work, [Emim][$EtSO_4$] and [Bmim][$MeSO_4$] ILs were studied. They are commercially available or could be easily prepared.[13] Their main physicochemical properties are shown in Table 1. From a consideration of their density and viscosity values, both ILs could be used as a solvent to desulfurate petrochemical products[14] and to extract organic chemicals[1,15] and contaminant gases.[16]

In this work, the thermal stability, effect of heating rate on the thermal properties, and characterization of the [Emim]-[$EtSO_4$] and [Bmim][$MeSO_4$] ionic liquids were analyzed.

Experimental

Ionic liquids 1-ethyl-3-methylimidazolium ethylsulfate ([Emim][$EtSO_4$], ≥ 95 % purity, from Sigma-Aldrich Chemie GmbH, water content was $2\cdot10^{-3}$ w/w, mass factor chloride < $3\cdot10^{-5}$) and 1-butyl-3-methylimidazolium methylsulfate ([Bmim][$MeSO_4$], ≥ 95 % purity, from Sigma-Aldrich Chemie GmbH, water content was $1\cdot10^{-3}$ w/w, mass factor chloride < $3\cdot10^{-5}$) were used. All experiments were carried out in a vacuum atmosphere

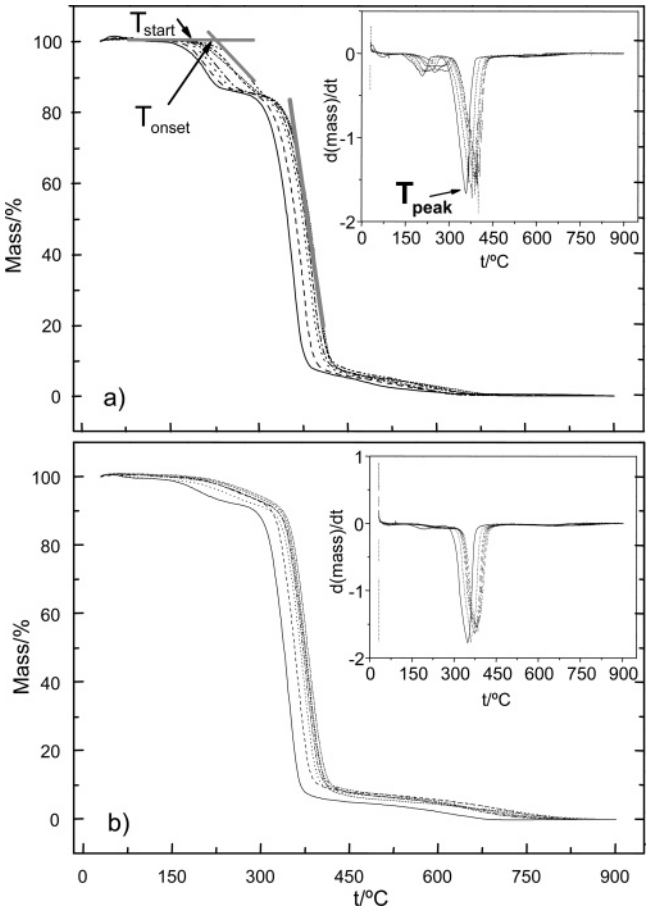

Figure 1. Effect of the heating rate, (—, 2; - - -, 4; • • •, 8; -•-•, 10; -••-••-, 12; —, 14; •••••, 16) °C·min^{-1} on the course of TGA scans for (a) [Emim][$EtSO_4$], indicating the start, onset, and peak temperatures, and (b) [Bmim][$MeSO_4$].

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Table 1. Physicochemical Properties of [Emim][$EtSO_4$] and [Bmim][$MeSO_4$] Given by the Manufacturer of These ILs (Sigma-Aldrich Chemie GmbH)

property	[Emim][$EtSO_4$]	[Bmim][$MeSO_4$]
molar mass/g·mol^{-1}	236.29	250.32
electric conductivity/μS·cm^{-1}	80 (25 °C)	20 (25 °C)
flash point/°C	162	102
inflammation point/°C	405	430
solubility in water	∞	∞
viscosity at room temperature/mPa·s	122.4	213.8
viscosity at 80 °C/mPa·s	14.3	19.1
density at at room temperature/g·cm^{-3}	1.2402	1.2129
density at 80 °C/g·cm^{-3}	1.2011	1.1748

glovebox under dry nitrogen due to the sensitivity of the ILs to humidity. The water content of every IL was determined by Karl Fischer titration (Mettler Toledo DL31). The mean of three replicate measurements was reported.

The thermogravimetric analyzer used in this work was a Mettler Toledo TGA/SDTA851^e. Two melting points (of indium and aluminum) and heating rates of (5, 10, and 20) °C·min^{-1} were used to calibrate the equipment. The accuracy of temperature and mass measurements was ± 0.1 °C and ± 10^{-3} mg, respectively. The TGA was utilized to measure several decomposition temperatures (T_{start}, T_{onset}, T_{peak}). The method used to calculate these temperatures is described in Figure 1a.[2,12] In the dynamic method, the temperature range was (30 to 900) °C at a heating rate of (2, 4, 8, 10, 12, 14, 16) °C·min^{-1} while purging with 70 mL·min^{-1} of dry nitrogen.[7] The mass of the sample in TGA analysis was from (4 to 12) mg. In the isothermal method, the temperatures tested were (50, 60, 70, 80, 120, 130, and 140) °C during 24 h. For every TGA analysis, aluminia pans (Al_2O_3) with a capacity of 70 μL were used.[7]

Differential scanning calorimetry was carried out on a Mettler Toledo DSC821^e. Depending on the thermal property to be determined, the DSC was calibrated according to the temperature range used and manufacturer's instructions.[17] The temperature measurements were carried out with an accuracy smaller than 0.1 °C. This technique was used to measure glass-transition, freezing, and melting temperatures of [Emim][$EtSO_4$] and [Bmim][$MeSO_4$][2,6] with a temperature range and heating and cooling rates equal to (−150 to 30) °C and 10 °C·min^{-1}, respectively. The heat capacities of ILs were determined with a 1 °C·min^{-1} heating rate between (10 and 100) °C. In every experiment, stainless steel pans with a volume of 120 μL and a purge flow of 50 mL·min^{-1} of dry nitrogen were used. The sample mass range used in DSC experiments was (17 to 23) mg.

Results and Discussion

Thermal Stability. For every IL tested by TGA, there are two ranges where the mass sharply decreases as temperature increases (Figure 1). In the first range, from (120 to 340) °C, the decomposition of both anions ([$EtSO_4$]$^-$ and [$MeSO_4$]$^-$) occurs. The decomposition of [Emim]$^+$ and [Bmim]$^+$ cations occurs from (275 to 450) °C. These data are in agreement with the literature.[13] In Holbrey's work, the temperature range, where the [Emim]$^+$ is decomposed [(350 to 400) K], is inside the degradation temperature range reported in this work [(275 to 450) K]. It is consistent with the purity of [Emim][$EtSO_4$] used

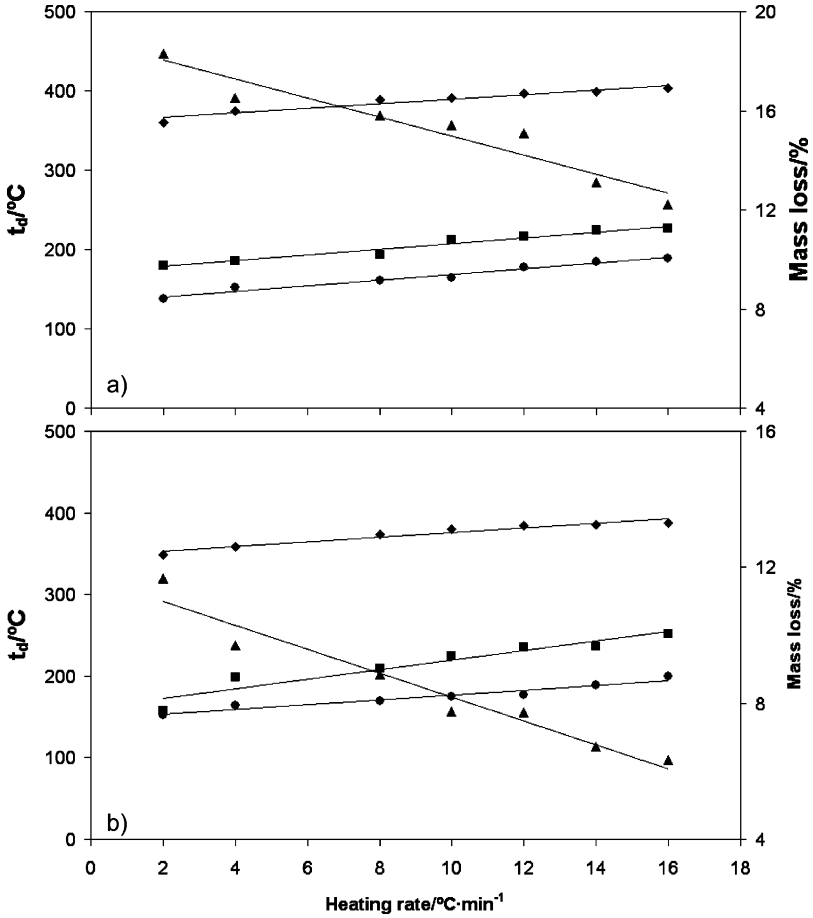

Figure 2. Decomposition temperatures and mass fraction loss. (a) [Emim][$EtSO_4$] (T_{onset}, $R^2 = 0.96$, $\sigma = 2.1$; T_{start}, $R^2 = 0.98$, $\sigma = 1.6$; T_{peak}, $R^2 = 0.92$, $\sigma = 2.4$; mass loss, $R^2 = 0.92$, $\sigma = 0.3$). (b) [Bmim][$MeSO_4$] (T_{onset}, $R^2 = 0.91$, $\sigma = 4.9$; T_{start}, $R^2 = 0.94$, $\sigma = 2.1$; T_{peak}, $R^2 = 0.93$, $\sigma = 2.3$; mass loss, $R^2 = 0.94$, $\sigma = 0.24$). ■, T_{onset}; ●, T_{start}; ▲, T_{peak}; ▲, mass loss.

Table 2. Glass Transition (T_g), Melting (T_{mp}), and Crystallization (T_c) Temperatures and Heat Capacities for Imidazolium ILs[a]

	T_g	T_{mp}	T_c	C_p
	°C	°C	°C	J·mol^{-1}·K^{-1} (25 °C)
[Emim][$EtSO_4$]	−78.4 ± 0.06 (−80.3 [20])	−	−	421.1 (378 [20])
[Bmim][$MeSO_4$]	−91.9 ± 0.06 (−92 [13])	−4.1 ± 0.06 (−5 [13])	-32.6 ± 0.06 (−34 [13])	255.3
[Bmim][Cl]	(−69 [2])	(41 [2])	−	
[Bmim][Br]	(−50 [2])	−	−	
[Emim][Tf_2N]	(−92 [2])	(−17 [2])	(−61 [2])	(524.3 [2])
[Emim][$MeSO_4$]	(−77 [13])	−	−	−
[Eeim][$EtSO_4$]	(−82 [13])	−	−	−
[Emim][$AlCl_4$]	−	(84 [21])	−	−
[Emim][NO_3]	−	(38 [22])	−	−
[Emim][PF_6]	−	(58 to 60 [22])	−	−
[Emim][dca]	(−104 [23])	(−21 [23])		
[Bmim][BF_4]	(−85 [2])	−	−	(351.5 [2])
[Bmim][PF_6]	(−76 [2])	(11 [2])	(−37 [2])	(397.6 [2])

[a] Literature values are included in parentheses.

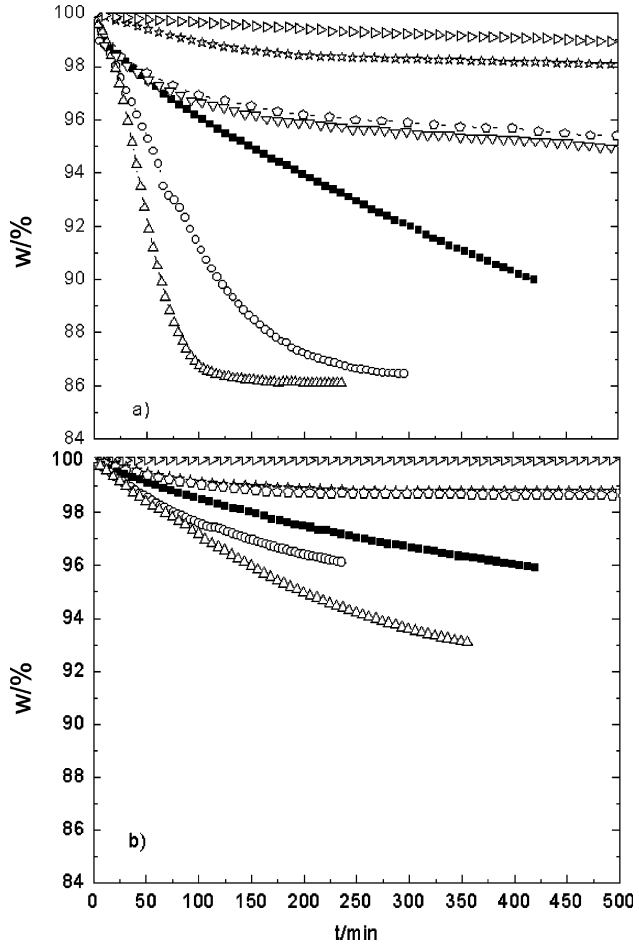

Figure 3. Isothermal TGA decomposition thermograms for [Emim][$EtSO_4$] and [Bmim][$MeSO_4$] ionic liquids depending on temperature: (open arrow pointing right, 50 °C; ☆, 60 °C; ⬠, 70 °C; ▽, 80 °C; ■, 120 °C; ○, 130 °C; △, 140 °C).

and synthesized by Holbrey et al. and the commercial IL used in this work, where more chemical impurities are present. As can be seen in Figure 1, there are no significant differences between the thermal stabilities of $[Emim]^+$ and $[Bmim]^+$ cations (less than 4 %).

The stability was evaluated by fast TGA scans. In Figure 1, the decrease of the IL mass with temperature at seven different heating rates is shown. The decomposition temperatures (T_{start}, T_{onset}, T_{peak}) increase with the heating rate. T_{peak} could be increased by 50 °C when the heating rate goes up from (2 to 16) °C·min^{-1}. Moreover, taking into account the decomposition temperature variation of [Emim][$EtSO_4$] and [Bmim][$MeSO_4$] ionic liquids with the heating rate (Figure 2), a linear relationship between their respective decomposition temperatures and the heating rate (r^2 higher than 0.9) has been found. These results confirm that the decomposition temperatures depend on the heating rate, and they are in agreement with the literature.[7,12] The discrepancies between the decomposition temperatures of ILs may lead to erroneous conclusions. Therefore, the decomposition temperature values cannot be calculated accurately by TGA dynamic analyses.[12] Given that it is necessary to know the maximum working temperature of ILs, an isothermal method was proposed.

On the other hand, the relative mass loss during the decomposition process in the temperature range (50 to 350) °C of both anions ($[EtSO_4]^-$ and $[MeSO_4]^-$) decreases as the heating rate increases (Figure 2). [Emim][$EtSO_4$] and [Bmim]-[$MeSO_4$] display mass fraction losses between (12 and 18 and 6 and 11) %, respectively. These losses correspond to (30 to 45) g·mol^{-1} and (14 to 26) g·mol^{-1}, respectively. They represent a slow thermal degradation of the anion to sulfate or hydrogensulfate.[13] When the heating rate is equal to 10 °C·min^{-1}, the T_{peak} and mass loss are comparable with values shown in the literature (differences are less than 4.5 % and 0.65 %, respectively).[13]

The isothermal TGA method was carried out for 24 h as a maximum, maintaining the temperature of the IL constant. During this time, the mass loss was measured (Figure 3). In every case, the thermogram consists of an initial sharply sloping portion followed by a linear step with a slope less than the previous one. The initial steep portion was used to characterize the thermal stability of ILs.[7]

The temperatures tested by the isothermal method were classified in two groups. In the first group, assuming that the real decomposition temperatures of the IL would be close to the smallest T_{start} (138.6 °C for [Emim][$EtSO_4$], 152.2 °C for [Bmim][$MeSO_4$]) taken from dynamical TGA runs (2 °C·min^{-1}), several temperatures near this, (120, 130, and 140) °C, were assayed. In the second group, values close to the temperature used in the manufacturing processes of ILs, specifically in the purification stage, (50, 60, 70, and 80) °C, were tested.[13] As can be seen in Figure 3, in the first group, the slopes increase with the temperature; i.e., where temperatures are (120 or 140) °C, the slope values are (−0.018 or −0.114) h^{-1} and (−0.006 or −0.018) h^{-1} for [Emim][$EtSO_4$] and [Bmim]-

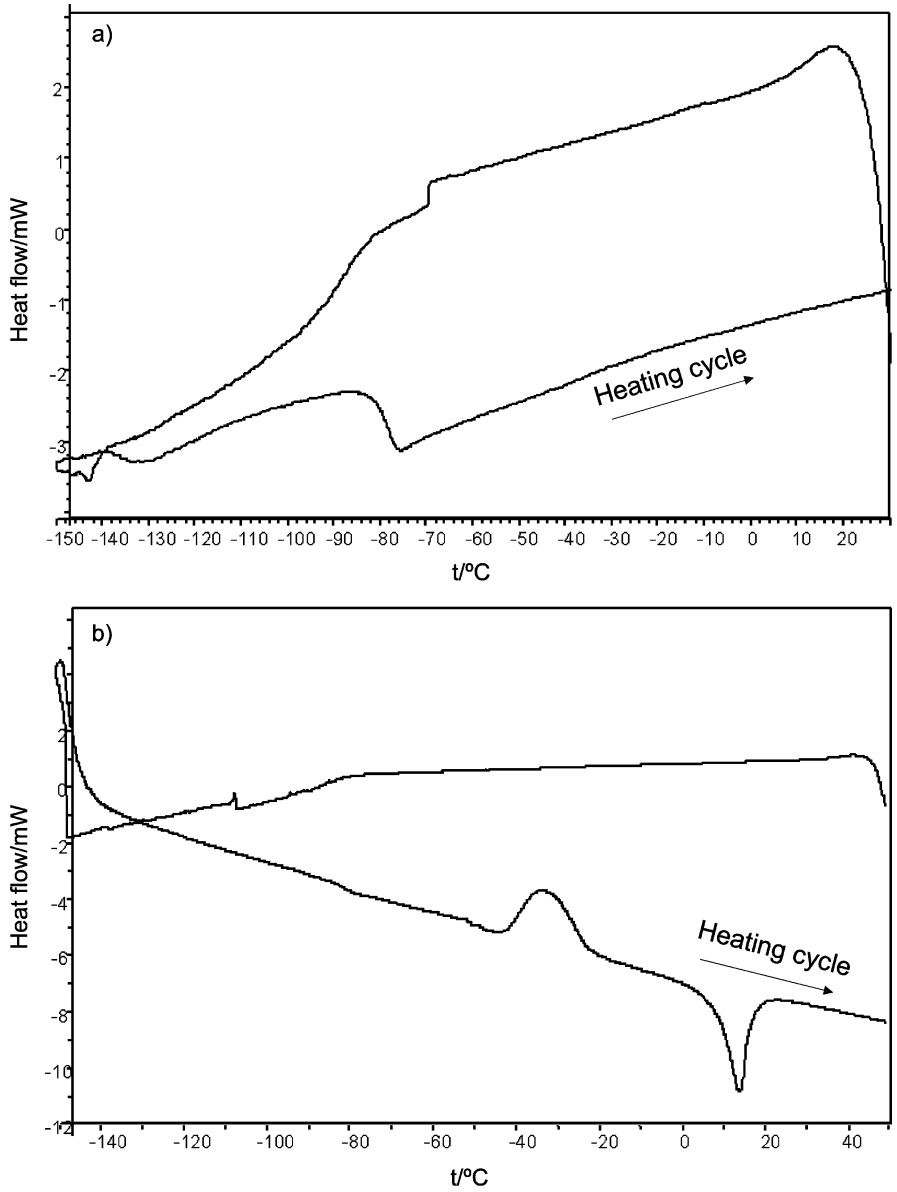

Figure 4. Differential scanning calorimetry results for (exo up) (a) [Emim][$EtSO_4$], showing only a glass-transition temperature around −80 °C, and (b) [Bmim][$MeSO_4$], showing glass-transition, crystallization, and melting point temperatures close to −80 °C, −30 °C, and 15 °C, respectively.

[$MeSO_4$], respectively. Therefore, they are thermally unstable. In the second group, when temperatures are equal to or less than 60 °C, the slope values are less than 0.0006 h^{-1}. By comparison with the slope values of the first group, this slope could be assumed as zero (Figure 3).[12] Consequently, both ionic liquids are thermally stable at temperatures and heating times less than 60 °C and 24 h, respectively.

Given that the difference between the smallest T_{start} (higher than 120 °C) and the temperature calculated by isothermal TGA experiments is close to 50 %, the stability of ILs cannot be calculated with accuracy by the decomposition temperatures obtained from dynamic TGA experiments. Moreover, taking our results into account, the isothermal TGA experiments may be a more proper method for evaluating the thermal stabilities of ILs.[12]

Thermal Properties. The calorimetric data of [Emim][EtSO4] and [Bmim][MeSO4] ILs were obtained by heating and cooling the sample in a DSC. As can be seen in Figure 4, [Emim]-[EtSO4] and [Bmim][MeSO4] have a glass-transition temperature at −78.4 °C and −91.9 °C, respectively. [Bmim][MeSO4] has a melting point and crystallization temperature of −4.1 °C and −32.6 °C, respectively, which are in agreement with the literature.[13] [Emim][EtSO4] has neither a melting nor a freezing temperature (Figure 4).[11] In the calculation process of the glass-transition temperature, the enthalpy jump difference between both ILs is due to the fact that [Bmim][$MeSO_4$] has an amorphous and crystalline structure (Tg and Tc) and [Emim]-[$EtSO_4$] has only an amorphous part (Tg).

As can be seen in Table 2, in most cases, the formation of glasses tends to be a general characteristic of the dialkylimidazolium ILs. Their Tg's are in the region (−100 to 100) °C for a wide range of anions and with alkyl chain lengths varying from ethyl to decyl.[13]

Heat Capacity. C_p values of [Emim][$EtSO_4$] and [Bmim]-[$MeSO_4$] measured by DSC[18] increase slightly with temperature as shown in eqs 1 and 2, respectively.

$$C_p/\mathrm{J{\cdot}g^{-1}{\cdot}K^{-1}} = -1.08 + 9.6{\cdot}10^{-3}{\cdot}T \quad (r^2 = 0.98;\ \sigma = 0.01) \quad (1)$$

$$C_p/\mathrm{J{\cdot}g^{-1}{\cdot}K^{-1}} = -1.39 + 8.1{\cdot}10^{-3}{\cdot}T \quad (r^2 = 0.95;\ \sigma = 0.07) \quad (2)$$

The C_p values were determined with a working temperature range between (10 and 100) °C because in this range no thermal events take place. As can be seen in Table 2, taking into account the molecular weight of ILs studied, the C_p values calculated at 25 °C are in agreement with C_p values given in the literature.[19,20] Compared to the literature, the C_p value at 298 K is higher than that reported by Zhang's work.[20] This difference (around 10 %) is due to the purity of [Emim][$EtSO_4$] (synthesized by the author) used by Zhang et al. and the commercial IL used in this work. Besides, Zhang's team used an adiabatic calorimeter to measure it. Otherwise, the C_p values reported in this work were calculated using the C_p of sapphire.[18]

Conclusions

Thermal properties of 1-ethyl-3-methylimidazolium ethylsulfate and 1-butyl-3-methylimidazolium methylsulfate ionic liquids have been established. The T_{start}, T_{onset}, and T_{peak} were measured by dynamic TGA runs. Given that the T_{start} varies with the heating rate, the decomposition temperatures of ILs were also measured by an isothermal TGA method. In this way, [Emim][$EtSO_4$] and [Bmim][$MeSO_4$] under 60 °C for 24 h are thermally stable. Given that the difference between this temperature and T_{start} is about 50 %, the dynamic TGA experiments are not appropriate to measure the thermal stability of ILs. Moreover, taking our results into account, the isothermal TGA experiments may be a more proper method for evaluating the thermal stabilities of ILs.

Using a DSC technique, the glass-transition temperatures of [Emim][$EtSO_4$] and [Bmim][$MeSO_4$] are equal to −78.4 °C and −91.9 °C, respectively. Inside the working range (−150 to 30) °C, [Emim][$EtSO_4$] has neither a melting nor a freezing temperature whereas [Bmim][$MeSO_4$] has both crystallization (−32.6 °C) and melting (−4.1 °C) temperatures. IL heat capacities were determined in the temperature range of (10 to 100) °C. In this, both ILs have a C_p value depending on temperature according to a linear function (correlation coefficients and σ for [Emim][$EtSO_4$] and [Bmim][$MeSO_4$] are equal to 0.98 and $\sigma = 0.01$ and 0.95 and $\sigma = 0.07$, respectively). This type of relationship is in agreement with the literature.[19,20]

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