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Thermal analysis of a ionic liquids family based on N,N-dialkylimidazolium

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ABSTRACT: *Ionic liquids are getting considerable interest because of their potential use as ecologic solvents, low volatility and thermal stability. The study of the thermal properties of a family of ionic liquids from N,N-dialkylimidazolium bromide, using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) is presented. Thermogravimetric studies reveal that ionic liquids decomposition occurs at high temperatures (>300°C) and thermal stability increases with increasing carbon substitution of the ring (from 319°C to 380°C). DSC shows the phase transitions, with changes in two or three phases, the transition temperature is affected by the symmetry of the molecule with an increase in this function.*

KEYWORDS: *ionic liquid, dialkylimidazolium, thermogravimetric analysis, differential scanning calorimetry.*

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I. INTRODUCTION

Ionic liquids (IL) were discovered in the early nineteenth century, when Walden, [1] synthesized the first ionic liquid at room temperature, ethylammonium nitrate with a melting point of 12°C. Sugden et al., [2] saw something they called "red oil" in a Friedel-Crafts reaction. Meanwhile, Hurley and Wier, [3] developed ionic liquids based chloroaluminate. The first generation of aluminum-containing ionic liquids are hygroscopic and sensitive to air. Therefore, these are not easy to handle. Wilkes and Zaworotko, [4] solved this problem with the use of new stable anions in air and water as halides, [PF6]- [BF4]- and [CF3CO2]-.

Cations commonly used in the process of obtaining ionic liquids are large and asymmetrical imidazolium derivatives [5, 6], pyridinium [7-9], pyrrolidinium [6], ammonium [10], phosphonium [11, 12] and sulfonium [13]. While anions are mostly inorganic molecules some of organic molecules are also used, such as halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate, among others and as for the organicosimidas, alkylsulfonate, alkylsulfate, p-toluenesulfonate, and trifluoroacetate, among others.5 Which generates a wide range of applications, derived from the physicochemical characteristics of each designed and synthesized ionic liquid [11, 14-19].

The physicochemical properties of ionic liquids can be adjusted by selecting a combination of anions and cations [20]. The general definition states that ionic liquids have a melting point below 100ºC [7, 9, 21]. The melting point of the large, non-symmetrical ions, whose charge can be distributed in a large volume is low and thus the melting point can be below 0°C. Moreover, the ILs don't evaporate as volatile organic compounds, and tend to decompose at high temperatures. The decomposition rate depends on each ionic liquid in particular on the anion finding more possible melting points between 300-400ºC [22]. In general, ionic liquids are miscible with polar solvents, but not with non-polar ones. The anion usually has a greater effect on the solubility than the cation, but is possible to make some modifications to the alkyl chains embedded to the cation, and the longer the chain the more non-polar character of the synthesized ionic liquid. The solubility in water is another important factor and varies with the anion. Most ionic liquids are not flammable and recyclable [23]. Stability can be evaluated in terms of chemical or thermal reactivity according to temperatures and reaction conditions the ILs are capable of supporting, and purity. The most common impurities are water and halides affecting the physical properties such as density, viscosity, melting point and degradation due to the temperature [6, 8, 9, 21, 24-26].

Furthermore, it is known that heteroatoms stability is determined by the strength of the carbon-heteroatom or heteroatom-hydrogen bonds and the ions that compose it an N-C bond is stronger than a N-H bond and consequently the stability of ammonium cations decreases in the following order: quaternary amine > tertiary > secondary > primary [27]. Gordon [10] in 1965 concluded that the quaternary ammonium and phosphonium salts are decomposed in a process of retro-quaternization or Hofmann elimination. Various authors report the measure of the degradation temperature using thermogravimetric analysis and differential scanning calorimetry [5-7, 9, 12, 21, 24-26, 28-31].

The thermal degradation tendency of different cations shows that the phosphonium cation is more stable than the imidazolium cation, and this on the other hand is more stable than the ammonium cation [32]. Imidazolium cation stability increases when the nitrogen and carbons in the ring have alkyl substituents [5]. The stability increases with linear chains compared to branched chains [33]. Thermogravimetric studies of different ionic liquids, showed the decomposition of the quaternary ammonium chloride at 150°C [20] the ones based on the imidazolium cation above 200ºC [5, 29] and the ones corresponding to the phosphonium cation at 300ºC [12, 34]. Ngo et al., [5] reported that ionic liquids stability depends on the anion, the more nucleophilic nature, the higher its tendency to react easily and quickly through a retro-quaternization reaction, and therefore, is less thermally stable. This means that ionic liquids containing weak acids are more resistant to thermal decomposition (1).

$$(C2F5SO2)N- < (CF3SO2)2N- < PF6- \approx BF4- < (CF3SO2)3C- \approx AsF6- \ll I-, Br-, Cl- \qquad (1)$$

Various authors [24, 35] reported degradation temperatures of 1-alkyl-3-methylimidazolium ionic compounds, found that the degradation temperature slightly increases when the alkyl chain is changed from ethane to octadecane, and the anion has a significant effect on the degradation temperature. Other authors36 reported melting points and swelling temperatures above 200°C.

This work focuses on the study of the thermal stability of bromide type of N,N-dialkylimidazolium ionic liquids, where the imidazolium cation is modified, with a substitution in both nitrogens with alkyl chains of 12 (D), 14 (T) and 16 (H) carbons asymmetrically and symmetrically; calorimetry and thermogravimetry.

II. MATERIALS AND METHODS

2.1 Synthesis of ionic liquid

Imidazolium salts were synthesized according to standard procedures published by several authors where the modifications vary in terms of the cations and/or anions used; and the synthesis conditions (Fig. 1) [37, 38, 39, 40, 41]. Table 1 shows the structures of the studied ionic liquids, considering the fact that the combinations of alkyl chains produce 3 pairs of equal compounds, which for thermal analysis purposes are suppressed.

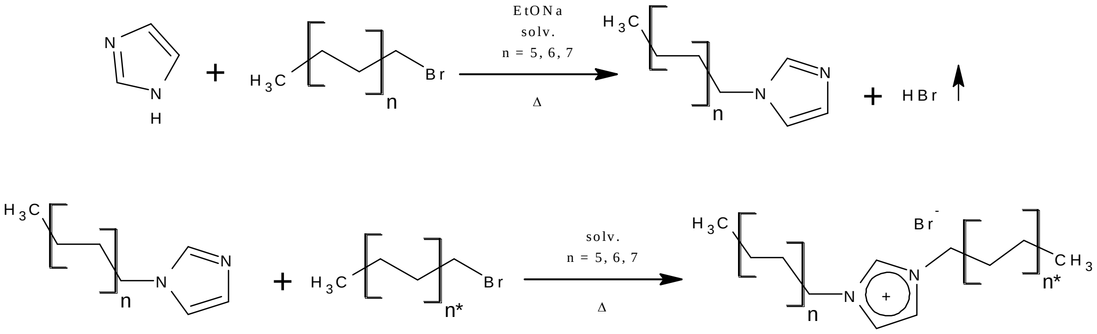
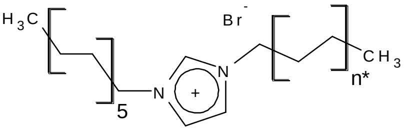
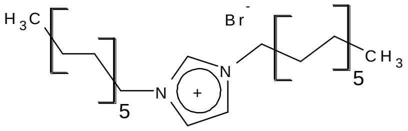
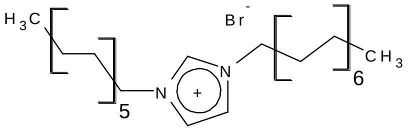
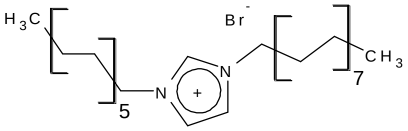
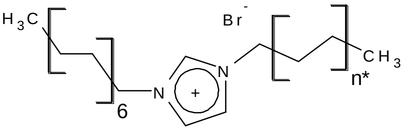
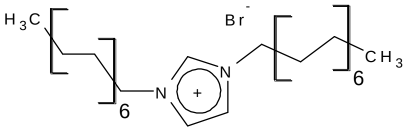
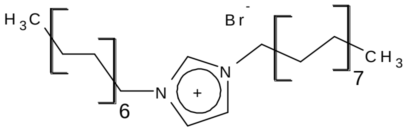
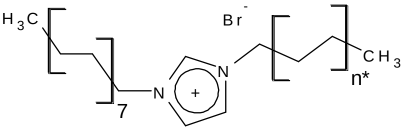
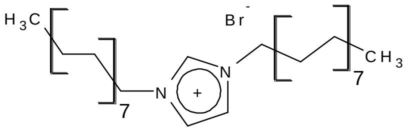


Fig. 1. Ionic liquids synthesis route.

2.2 Thermogravimetric analysis (TGA)

A compositional analysis by thermogravimetry with the ASTM E-1131-08 method in a thermogravimetric Analyzer (Perkin Elmer, model-7HT TGA) was performed in a range of 25°C to 600°C at 5°C min^{-1}, with a nitrogen purge Praxair Brand 99.999% purity and a flow of 20 mL min^{-1}.

Table 1. Chemical formula and structure of ionic liquids.

Ionic Liquid	n* = 5, 6, 7	Structure, name and abbreviation	Entry
 **$[C_{12}H_{25}(N_2C_3H_3)CH_2(C_2H_4)_{n*}CH_3]$ [Br]**	$CH_3(C_2H_4)_5CH_2Br$	 1,3-didodecylimidazolium bromide [1D3DIM][Br]	1
	$CH_3(C_2H_4)_6CH_2Br$	 1-dodecyl-3-tetradecylimidazolium bromide [1D3TIM][Br]	2
	$CH_3(C_2H_4)_7CH_2Br$	 1-dodecyl-3-hexadecylimidazolium bromide [1D3HIM][Br]	3
 **$[C_{14}H_{29}(N_2C_3H_3)CH_2(C_2H_4)_{n*}CH_3]$ [Br]**	$CH_3(C_2H_4)_5CH_2Br$	[1D3TIM][Br]	4
	$CH_3(C_2H_4)_6CH_2Br$	 1,3-ditetradecylimidazolium bromide [1T3TIM][Br]	5
	$CH_3(C_2H_4)_7CH_2Br$	 1-tetradecyl-3-hexadecylimidazolium bromide [1T3HIM][Br]	6
 **$[C_{16}H_{33}(N_2C_3H_3)CH_2(C_2H_4)_{n*}CH_3]$ [Br]**	$CH_3(C_2H_4)_5CH_2Br$	[1D3HIM][Br]	7
	$CH_3(C_2H_4)_6CH_2Br$	[1T3HIM][Br]	8
	$CH_3(C_2H_4)_7CH_2Br$	 1,3-dihexadecylimidazolium bromide [1H3HIM][Br]	9

2.3 Analysis by differential scanning calorimetry (DSC)

The scanning calorimetry was used for the synthesized ionic liquids characterization, using the ASTM E-794-06 method in a differential scanning calorimeter (Perkin Elmer DSC-7) in a range from 25°C to 500°C at

5°C min^{-1} and a nitrogen purge Praxair Brand 99.999% purity with a flow of 20 mL min^{-1}. Getting the thermal characteristics reported.

III. RESULTS AND DISCUSSION

Thermal stability analysis, by thermogravimetry. In Figure 2, a thermogram for the matrix used in the synthesis imidazolium [IM], el blanco 1-methylimidazolium [1MIM] and an ionic liquid [1H3HIM][Br] model is presented, the variation of the sample mass as a function of the increase in the applied temperature is observed, obtaining the decomposition temperature ($T_{decomposition}$) and the degradation sequence of the molecules studied.

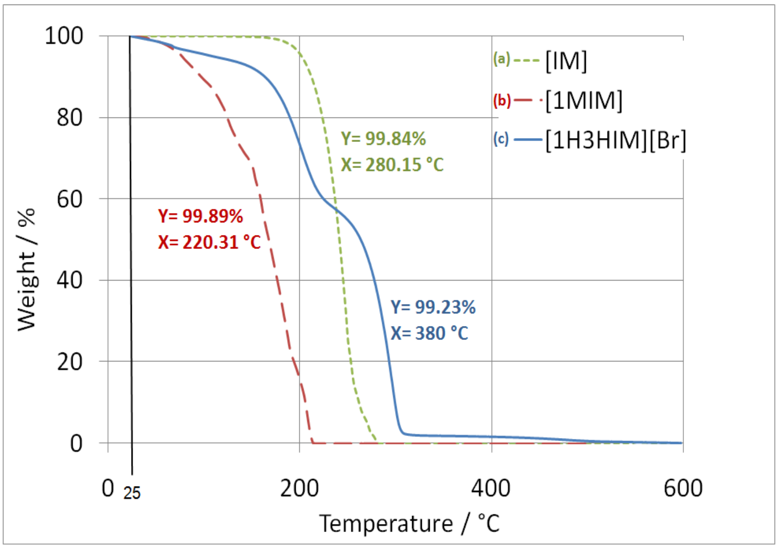


Fig. 2. Thermal analysis of the matrix synthesis (a) [1MIM] and (b) the ionic liquid.

Thermal decomposition (T_{dec}) of ionic liquids depends on the structure of the ionic compound. By increasing the size of the substitution chains on the imidazolium cation thermal stability increases due to the hydrogen substitution on the ring by larger structures such that [1MIM] (Fig. 2(b) matrix synthesis) shows a T_{dec}= 220.31°C, and the [1D3DIM][Br] (twelve carbon substitution) presents a T_{dec}= 319.96°C, the [1T3TIM][Br] (fourteen carbon substitution) shows a T_{dec}= 349.85°C and finally the [1H3HIM][Br] (figure 2(c) sixteen carbon substitution) with a T_{dec} = 380°C (Table 2 and Fig. 3 a-c).

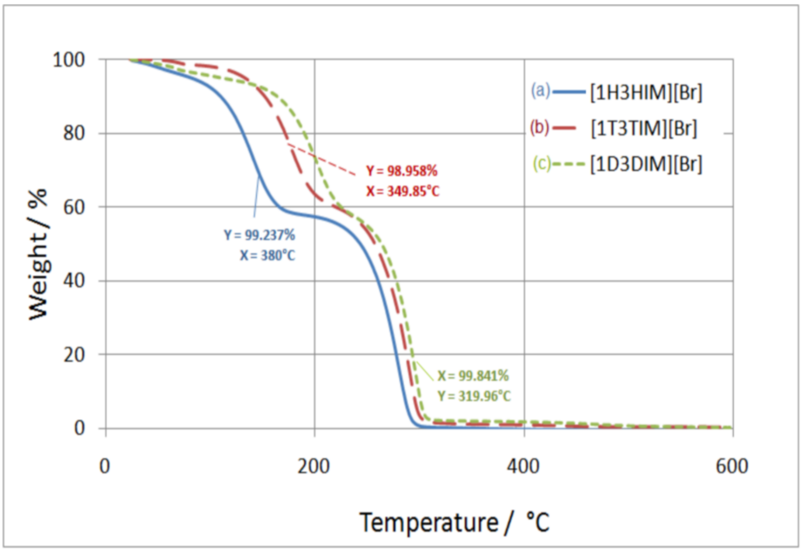


Fig. 3. Thermal analysis of the ionic liquid (a) [1D3DIM][Br], (b) [1T3TIM][Br] and (c) [1H3HIM][Br].

Table 2. Obtained data from thermal analysis (TGA) for the Imidazolium [IM], 1-Methylimidazolium [1MIN] and the N, N-dialkylimidazolium synthesized ionic liquids.

Ionic Liquid	Decomposition temperature, T_{dec} / (^{0} C ± 0.5)
[IM]	280.00
[1MIM]	220.31
[1D3DIM][Br]	319.96
[1D3TIM][Br]	330.11
[1D3HIM][Br]	349.94
[1T3DIM][Br]	ND
[1T3TIM][Br]	349.85
[1T3HIM][Br]	380.00
[1H3DIM][Br]	ND
[1H3TIM][Br]	ND
[1H3HIM][Br]	380.00

Furthermore, the molecules asymmetry doesn't seem to have a distinct tendency in the decomposition temperatures when working with molecules of high carbon number (14 and 16 carbons) this because progressive increases in temperature are not observed in terms of the carbon substitution number (Table 2). However, in the case of ionic liquids with 12 carbon substitutions in the nitrogen 1 (N1) there is an increase of the decomposition temperature with increasing carbon number substituted on the nitrogen ([1D3DIM][Br] < [1D3TIM][Br] < [1D3HIM][Br]) (Fig. 4).

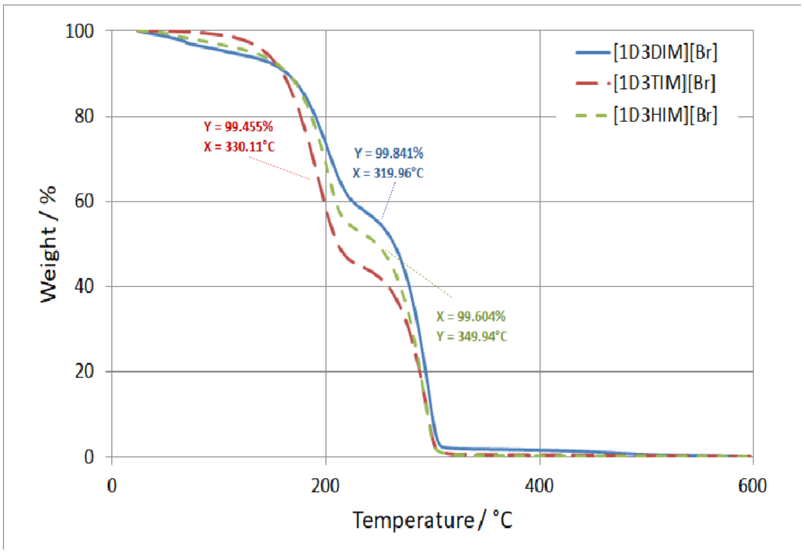


Fig. 4. Thermal analysis of the ionic liquids (a) [1D3DIM][Br], (b) [1D3TIM][Br] and (c) [1D3HIM][Br].

One could attribute this to the physical state of the analyzed samples, while the 12 carbons in N1 ionic liquids are liquid, on the N3 regardless replacement, the rest of the synthesized products are gels whose physical appearance seems to solidify with changes of the chain size.

Change of the transition state analysis, by differential scanning calorimetry.

In Figure 5, the differential scanning calorimetry thermogram for the matrix used in the synthesis [1MIM] and an ionic liquid [1H3HIM][Br] model is presented, the variation of the heat emitted by the sample as a function of the increase in the applied temperature is observed, the change or transition temperature (T_{onset}), the transition energy (ΔH J g^{-1}) and the curve of the derivative, were obtained.

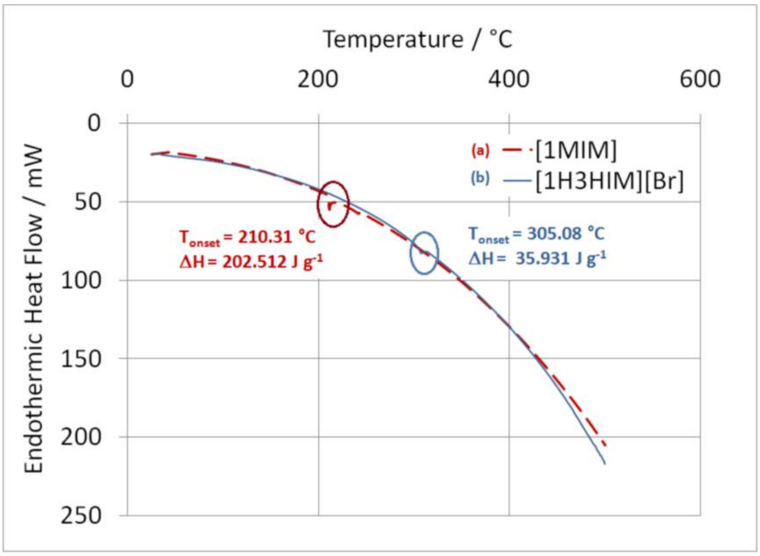


Fig. 5. Differential Scanning Calorimetry of the matrix synthesis (a) [1MIM] and (b) the ionic liquid [1H3HIM][Br].

Calorimetric data was obtained by heating the sample at 25-500°C (Table 3). The transition or phase change temperatures (T_{onset}) in ionic liquids can be affected the symmetry of the structure of the cation, so that there is an increase of this temperature as a result of a higher symmetrical molecule (Figure 6), as in the case of [1D3DIM][Br] T_{onset} = 287.33°C which has two alkyl chains of twelve carbons each, the [1D3TIM][Br] T_{onset} = 290.94°C which has a chain of fourteen and another of twelve carbons, and [1D3HIM][Br] T_{onset} = 306.24°C with a chain of twelve and another of sixteen carbons, these three ionic liquids are in liquid phase, the temperature differences between these molecules are not great but these are significant since the physical state of some of the samples analyzed undergo a change of liquid-gas state, while others experience the three gaseous-liquid-solid phase changes for the liquid-gas phase change, in case it occurs, it is observed at low temperatures, lower than 40°C, this corroborated by other authors [40].

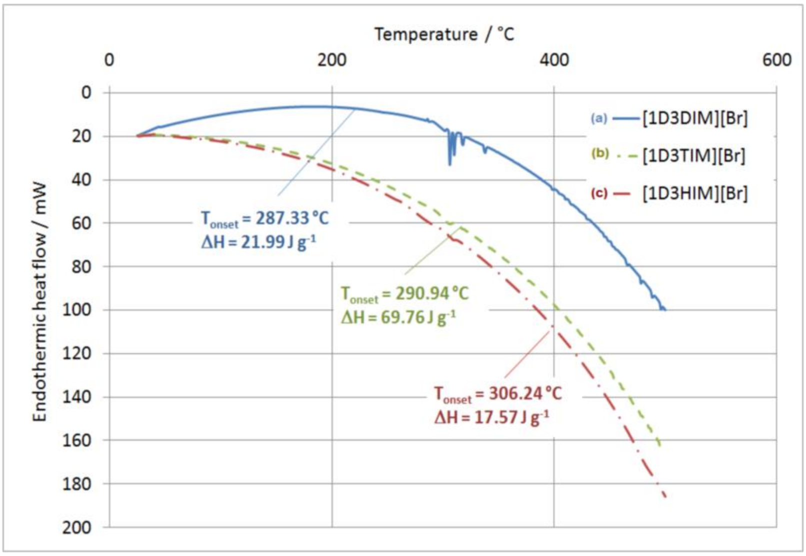


Fig. 6. Differential Scanning Calorimetry of the ionic liquids (a) [1D3DIM][Br], (b) [1D3TIM][Br] and (c) [1D3HIM][Br].

It is also possible to observe the effect of the size of the molecule at the transition temperature, where the increase in size provides an increase in the temperature, as in the case of [1MIM] T_{onset} = 210.31°C, [1D3DIM][Br] T_{onset} = 287.33°C, [1T3TIM][Br] T_{onset} = 289.93°C and [1H3HIM][Br] T_{onset} = 305.08°C (Figure 7). ΔH transition values are low (<71.57 J g^{-1}), which is characteristic of ionic molecules with endothermic behavior [5, 11]. Moreover imidazolium [IM] and 1-methylimidazolium [1MIM] possess high transition energies 182.764 and 202.512 J g-^{1} respectively.

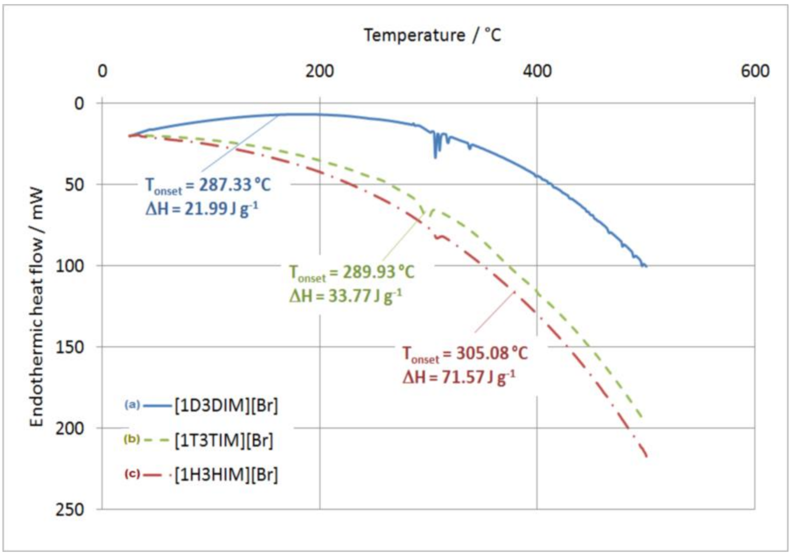


Fig. 7. Differential Scanning Calorimetry of the ionic liquids (a) [1D3DIM][Br], (b) [1T3TIM][Br] and (c) [1H3HIM][Br].

Imidazolium is a non auto-oxidation and very stable compound, solid at room temperature and 1-methylimidazolium is a liquid, both soluble in water (polar). Their boiling points are high 256 and 198°C respectively (Table 3) likewise the T_{onset} 291.86 and 210.31°C (Table 3), this can be attributed to the resulting strong dipole association from the imidazolium and 1-methylimidazolium structures (tautomerism), and in addition the imidazolium shows an increase in thermal stability as a result of intramolecular hydrogen bonding [42]. Moreover ionic liquids synthesized from these are compounds exclusively consisting of ions with the main feature of being asymmetric and so large that the cation-anion attractive forces are weaker than the forces involved in the formation of their precursors. Just a small energy input is necessary to remove the cations and anions that make up the ionic liquid and to produce a change in phase.

Table 2. Transition or phase change temperature data (T_{onset}) and ΔH (J g^{-1}), obtained by differential scanning calorimetry (DSC) for the Imidazolium [IM], 1-Methylimidazolium [1MIM] and *N,N*-dialkylimidazolium ionic liquids.

Ionic Liquid	T_{onset} / (^{0} C ± 0.5)	ΔH / (J g^{-1})
[IM]	2991.86 (256*)	182.76
[1MIM]	210.31 (198*)	202.51
[1D3DIM][Br]	287.33	21.99
[1D3TIM][Br]	290.94	69.76
[1D3HIM][Br]	306.24	71.57
[1T3DIM][Br]	ND	ND
[1T3TIM][Br]	289.93	33.77
[1T3HIM][Br]	275.53	43.67
[1H3DIM][Br]	ND	ND
[1H3TIM][Br]	ND	ND
[1H3HIM][Br]	305.08	35.93

* The reported temperatures 256 and 198°C for the [IM] and [1MIN] respectively correspond to the boiling points of the commercial products.

The synthesized ionic liquids show a variety of applications, however the high thermal stabilities observed in this study allow the application of these molecules in the more recent oil industry processes, in-situ process which seek to improve the extraction and transport of oil in pipelines in a more efficient and economical way, where high temperatures and extraction pressures are involved, which may well modify the physicochemical properties of the known ionic liquids [43].

IV. CONCLUSIONS

This paper is the first part of a project which aims to explore the application of ionic liquids for an improvement of the Mexican crude oil transportation properties, transition temperatures and decomposition, some of the most important parameters are associated to the working pressure, which allow to consider this type of compounds as potential modifiers of viscosity (cP) and / or °API crude.

With the conducted TGA studies it is possible to conclude that the size of the cation substitution in the imidazolium increases the thermal stability of ionic liquids, in a such way that for symmetrical molecules the decomposition temperatures observed were of 220.31°C [1MIM] < 319.96°C [1D3DIM][Br] < 349.85°C [1T3TIM][Br] < 380°C [1H3HIM][Br]. As for the asymmetryc molecules, an increase in the decomposition temperature for the substitutions of 12, 14 and 16 carbons in the 1-D-3-alkylimidazole ionic liquids was observed, 319.96°C [1D3DIM][Br] < 330.11°C [1D3TIM][Br] < 349.94°C [1D3HIM][Br], this tendency is not presented in molecules with larger alkyl chains. In transition temperatures (T_{onset}) the differences in these molecules are not large but they are significant given the change in the physical state. Increasing the size of ionic liquid provides an increase in the temperature 210.31°C [1MIM] < 287.33°C [1D3DIM][Br] < 289.93°C [1T3TIM][Br] < 305.08°C [1H3HIM][Br]. ΔH transition values are low 71.57 J g^{-1}, characteristic of endothermic systems.

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