

## SYNTHESIS AND THERMAL PROPERTIES OF TWO NEW DICATIONIC IONIC LIQUIDS

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### ABSTRACT

Two new dicationic ionic liquids 1,7-bis(3-methylimidazolium-1-yl)heptane bromide (I) and 1,8-bis(3-methylimidazolium-1-yl)octane bromide (II) have been synthesized and characterized by elemental analysis, FT-IR, <sup>1</sup>H and <sup>13</sup>C NMR, and TG-DSC techniques. The compound (I) is liquid at room temperature, whereas (II) is liquid at 42.7°C.

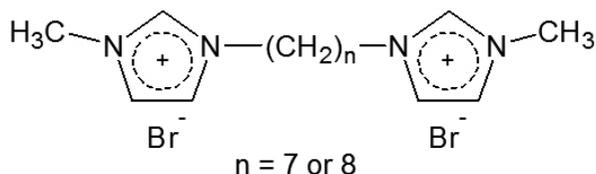
**Keywords:** Dicationic Ionic liquids, thermal properties, synthesis.

### INTRODUCTION

Ionic liquids (ILs) have been recognized as potential new green alternatives to conventional organic solvents in a wide range of synthetic, catalytic, separation and electrochemical applications. They are characterized by their unique physicochemical properties, including low melting points, low flammability, and tunable hydrophobicities. They are stable in a wide range of temperature, and have great chemical and electrochemical stability. In addition, they have negligible vapor pressures so there is no loss of solvent through evaporation, avoiding environmental problems due to volatilization<sup>1-5</sup>.

The dicationic ionic liquids contain two head groups, linked by a rigid or flexible spacer<sup>6</sup>. This kind of ILs demonstrate unique features in critical micelle concentration, better behavior as lubricants, electrolytes characteristics, surface tension, and higher thermal stabilities than monocationic ILs and other traditional solvents<sup>6,9</sup>. Besides the combination cation-anion, simple changes in the length of the spacer or in the aliphatic chains on the cations, allows the physical properties of these ionic liquids to be tailored for specific applications<sup>11-13</sup>.

We report here, the synthesis, characterization and thermal properties of two new dicationic ionic liquids. The general molecular structure of these compounds is shown in figure 1.



**Figure 1:** Structure of the new synthesized dicationic ionic liquids.

### EXPERIMENTAL

All materials were purchased from Sigma-Aldrich and used without any additional purification.

NMR experiments were carried out on a Bruker Avance 600 spectrometer operating at 600.23 MHz. NMR spectra were recorded at 27°C with the HDO signal used as an internal reference ( $\delta$  4.70 at 27°C). The compounds were dissolved in 500  $\mu$ L (90% H<sub>2</sub>O / 10% D<sub>2</sub>O). Watergate pulse sequences<sup>10</sup> were used to suppress the proton signal of the solvent. FT-IR was recorded on a Nicolet Avatar 330 spectrophotometer using KBr pellets. Elemental analysis (C, H, N) was performed on a Carlo Erba EA 1108 instrument and the mass spectra were recorded on a VG AutoSpec FISON spectrometer.

Dynamic thermogravimetric measurements were performed using a Mettler TG/SDTA 851<sup>e</sup> thermobalance. The thermogravimetric results were

processed by Mettler calorimetric system using the Start<sup>e</sup> program system. Samples were heated in Al<sub>2</sub>O<sub>3</sub> pans. Measurements were carried out between 0°C and 900°C at 20° min<sup>-1</sup> under N<sub>2</sub>.

The calorimetric measurements DSC reported were carried out at a 20K/ min heating rate in a Mettler 821 calorimetric system, using Start<sup>e</sup> program system; the temperature scale was calibrated using indium. The typical amount of sample was 20 mg.

The new compounds were synthesized by the following process: **1,7-bis(3-methylimidazolium-1-yl)heptane bromide (I)**. A mixture of 1-methylimidazole (0.25 mol) and 1,7 dibromoheptane (0.05mol) were heated at 80°C and stirred for 48 h under dry argon atmosphere. After a slow cooling of the reaction system to room temperature, a yellow oil was separated and washed three times with acetone and then dried under vacuum. Compound (I) was obtained as a viscous yellow oil, with 62.1% of yield. <sup>1</sup>H NMR:  $\delta$  = 8.61 (H-2), 7.37 (H-1), 7.32 (H-3), 4.08 (H-4), 3.78 (H-5), 1.74 (H-6), 1.25 (H-7), 1.12 (H-8), Fig. 4. <sup>13</sup>C NMR:  $\delta$  = 135.7 (C-2), 123.5 (C-1), 122.1 (C-3), 49.4 (C-4), 35.7 (C-5), 29.1 (C-6), 27.5 (C-7), 25.1 (C-8). IR (400-4000 cm<sup>-1</sup>, pellet KBr): 3087 [ $\nu$ (Ar-H)]; 2859 [ $\nu$ (C-H)]; 1463 [ $\nu$ (C=N)]; 1168 [ $\nu$ (C-N)]; 1573 [ $\nu$ (C=C)]. Elemental analysis calculated (%) for C<sub>15</sub>H<sub>30</sub>N<sub>4</sub>Br<sub>2</sub> · H<sub>2</sub>O: C 40.93; H 6.41; N 12.73. Found: C 41.31; H 6.89; N 13.16. **1,8-bis(3-methylimidazolium-1-yl)octane bromide (II)**, it was synthesized by similar procedure described above and was obtained as a white solid. Yield 93.3%. <sup>1</sup>H NMR:  $\delta$  = 8.59 (H-2), 7.35 (H-1), 7.31 (H-3), 4.06 (H-4), 3.77 (H-5), 1.73 (H-6), 1.18 (H-7, H-8), Fig. 5. <sup>13</sup>C NMR:  $\delta$  = 135.7 (C-2), 123.4 (C-1), 122.1 (C-3), 49.5 (C-4), 35.6 (C-5), 29.1 (C-6), 27.8 (C-7)\*, 25.2 (C-8)\* \*exchangeable. IR (400-4000cm<sup>-1</sup>, pellet KBr): 3141 [ $\nu$ (Ar-H)]; 2930 [ $\nu$ (C-H)]; 1463 [ $\nu$ (C=N)]; 1167 [ $\nu$ (C-N)]. Elemental analysis calculated (%) for C<sub>16</sub>H<sub>38</sub>N<sub>4</sub>Br<sub>2</sub> · H<sub>2</sub>O: C 43.66; H 7.33; N 12.73. Found: C 42.31; H 6.66; N 12.33.

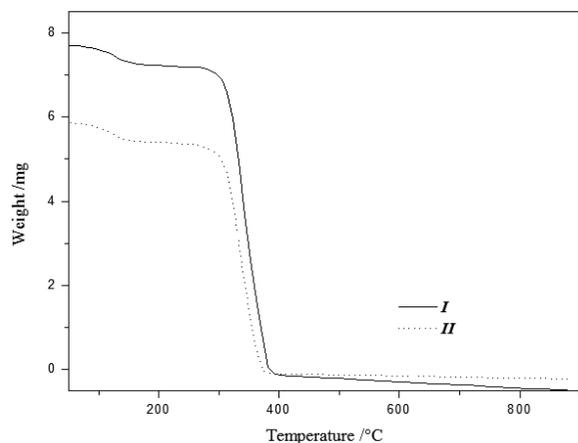
### RESULTS AND DISCUSSION

Thermogravimetric (TG) analysis experiments were conducted to determine the thermal stabilities of the novel ILs. As shown in Figure 2, the decomposition temperature (T<sub>d</sub>) for the sample (I) is 343°C and the T<sub>d</sub> for sample (II) is 338°C, it is clearly that 1,7-bis(3-methylimidazolium-1-yl)heptane bromide has better thermal stability than 1,8-bis(3-methylimidazolium-1-yl) octane bromide.

The TG curves of (I) and (II), shown in Figure 2, shows a single weight loss for both compounds between 25 and 130 °C of 4.6% and 4.8% of the original weight, corresponding to the loss of one water molecule for (I) and (II). In both compounds, the TG traces decreased abruptly around 330°C and above, corresponding to evaporation for (I) and sublimation in case of (II), this also means the start of decomposition.

Information about thermal stabilities of dicationic ionic liquids is scarce, except for some studies<sup>11,14,18,19</sup>. Generally, thermal stabilities of dicationic ionic liquids are significantly higher than their monocationic analogues due to their higher charge, higher molecular weight, and greater intermolecular interactions<sup>18</sup>.

Literature reports indicate that the thermal decomposition is strongly dependent on salt structure. Normally in monocationic ionic liquids, increasing the substitution alkyl chain of the imidazolium cation, increases the thermal stability<sup>17</sup>. However, it seems that for dicationic ionic liquids the length of the linkage chain increase the thermal stability<sup>14</sup>. Although molecules of water were found in this work, comparing with a previous report, where the substitution alkyl chain is very long, but the linkage chain is short (1,4-bis(3-tetradecylimidazolium-1-yl) butane bromide<sup>8</sup>), the decomposition temperature found is 303.5°C, and in this work the decomposition temperatures are significantly higher, 338 and 343°C for **(I)** and **(II)** respectively.



**Figure 2:** Thermogravimetric curve for Ionic Liquids **(I)** and **(II)**.

The DSC heating and cooling curves for compound **(I)** and **(II)** are illustrated in Figures 3a and 3b, respectively. In heating, the compound **(I)** present two distinct exothermic transitions, an exotherm crystallization temperature ( $T_c^h$ ) preceding the melting temperature ( $T_{s-l}^h$ ). In the cooling curve, there is a single peak corresponding to a solid-solid transition ( $T_{s-s}^c$ ). The compound **(II)** shows a solid-solid transition ( $T_{s-s}^c$ ) before the melting point ( $T_{s-l}^h$ ). In the cooling scan there is a solid-solid transition ( $T_{s-s}^c$ ), which is displaced of the heating transition implying an amorphous compound.

In addition, enthalpies for each thermal transition were calculated, and are shown in Table 1.

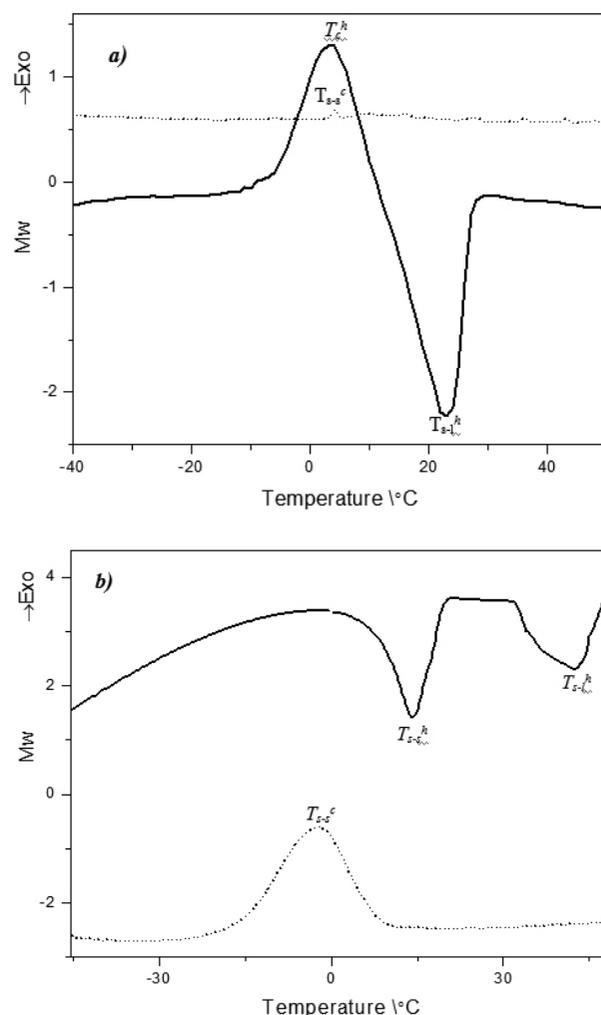
**Table 1:** Phase transitions and enthalpies.

Ionic Liquid I			Ionic Liquid II		
	T/[°C]	$\Delta H$ /[J/mol]		T/[°C]	$\Delta H$ /[J/mol]
$T_c^h$	3.03	-8.17E-3	$T_{s-s}^h$	14.67	1.36E-2
$T_{s-l}^h$	22.94	7.40E-3	$T_{s-l}^h$	42.67	2.50E-2
$T_{s-s}^c$	3.8	4.77E-4	$T_{s-s}^c$	-4	7.70E-3

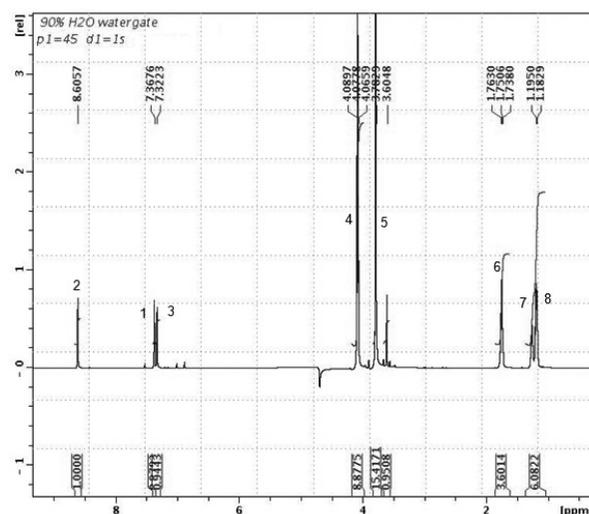
<sup>h</sup> Heating

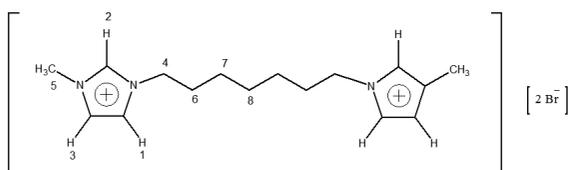
<sup>c</sup> Cooling

Both compounds had a  $T_{s-l}$  below 100°C, which could be considered as ILs. For **(I)** the solid-liquid transitions occurs at 22.9°C, being liquid at room temperature, however **(II)** has a solid-liquid transition at 42.7°C. This behavior is contrary to what was expected, since increasing the link chain between the cations, the solid-liquid transition should decrease<sup>12,14</sup>. This phenomenon could be related to the water molecules present in both products.

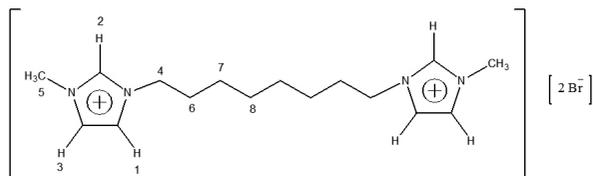
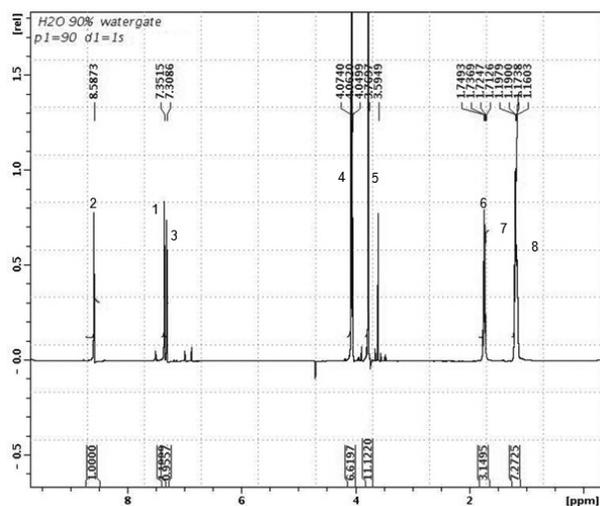


**Figure 3:** Differential Scanning Calorimetry curves, a) Ionic Liquid **(I)**, b) Ionic Liquid **(II)**





**Figure 4:** <sup>1</sup>H NMR, 1,7-bis(3- methylimidazolium-1-yl)heptane bromide (I).



**Figure 5:** <sup>1</sup>H NMR, 1,8-bis(3- methylimidazolium-1-yl)octane bromide (II).

### CONCLUSIONS

In summary, we presented the synthesis of two new dicationic ionic liquids, 1,7-bis(3-methylimidazolium-1-yl)heptane bromide and 1,8-bis(3-methylimidazolium-1-yl)octane bromide, with a simple procedure and obtaining products with high yields. In addition, a complete spectroscopic and thermal analysis was made for both compounds. Both compounds show the presence of water molecules, but this solvent only change slightly the thermal properties of the new ionic liquids reported here, with respect to related unsolvated ILs.

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