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Complete List of Authors:	Lorenzo, Marta; University of Vigo, Química Orgánica Vilas, Miguel; University of Vigo, Química Orgánica Verdía, Pedro; University of Vigo, Química Orgánica Villanueva, María; University of santiago de Compostela, Salgado, Josefa; University of santiago de Compostela, Tojo, Emilia; University of Vigo, Organic Chemistry

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Long-Term thermal stabilities of ammonium ionic liquids designed as potential absorbents of ammonia†

M. Lorenzo,[a] M. Vilas,[a] P. Verdía,[a] M. Villanueva,[b] J. Salgado[b] and E. Tojo*[a]

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Searching for potential absorbents in working pairs with NH_3, a series of new ammonium ionic liquids related to choline were designed and synthesized. In order to explore their applicability in refrigeration by absorption, their thermal stabilities were studied. For this proposal, a thermogravimetric analyzer, TGA 7- Perkin Elmer, was used in dynamic mode from 100 ºC to 800 ºC at 10 ºC/min under dry air atmosphere. From the ionic liquids TG curves, the onset temperatures (T_{onset}) were determined, as well as the loss of mass at these T_{onset}. Significant decomposition was detected at lower temperatures than T_{onset} in all cases, meaning that the true ionic liquids stability is lower than that provided by the dynamic TG. Isothermal studies at lower temperatures than T_{onset} were also carried out to estimate the long-term thermal stabilities at different temperatures.

Introduction

Ionic Liquids (ILs), defined as salts that melt below 100 ºC, have gained increasing importance both in the scientific and industrial engineering community during last decade. Due to their remarkable and interesting properties, such as negligible vapor pressure, non-flammability, high polarity, wide range temperature in liquid phase, and high thermal stability, ILs are finding widespread use as engineering fluids.[1] Their properties report a high potential as "green absorbents" and recently, ILs are being investigated as possible absorbents for the refrigeration by absorption in order to present an alternative to the conventional working fluid pairs used in absorption machines.[2] One of this fluids is the refrigerant (a highly volatile liquid) and the other one is the absorbent, which must be no-volatile. Both fluids must be thermally and chemically stable at the working temperature range and the difference between their vaporization temperatures must be greater than 150 K. Other important requirements are: low viscosity, high thermal conductivity, low specific heat capacity, large vaporization enthalpy, and negative deviations from Raoult's law.

Many of the works on ILs as absorbents are focused on developing new working pairs of natural refrigerants such as NH_3, H_2O or CO_2, with ILs to replace LiBr in absorption chillers or in heat exchangers.[3] Special attention has attracted the use of ILs as absorbents of natural ammonia refrigerant.[4]

Although a large number of ILs have been prepared and characterized to date, many of them are based on cations or anions that limit their application due to toxicological, ecological or economic reasons. To avoid these drawbacks, the use of ILs derived from biomaterials such as the essential nutrient derived from ammonium namely choline is highly recommended.[5] For example, it is known that choline cation leads to relatively benign ILs with proteins stabilization characteristics.[6] On the other hand, no many new green absorbents based on ILs derived from ammonium have been characterized, so their application in absorption machines is very limited by the scarce knowledge that there is about them. Thus, studies on the design, synthesis and characterization of new absorbents based on ammonium ILs, are needed.

Besides toxicity, another criterion that must be considered when selecting an IL for a specific application is its thermal behaviour. Thermal stability is a key property for industrial applications.[7] High thermal stability increases the performance of industrial processes and improves operational safety avoiding undesired corrosive and toxic products. In addition, ILs applications often require extended operations at different temperatures; therefore, it is essential to determine the thermal stabilities of the ILs and also the time of degradation at working temperatures.

In this work eight new ammonium ILs related to choline, were designed and synthesized as potential absorbents of natural ammonia refrigerant. In addition, their thermal stability is analysed because it is one of the main conditions that an absorbent must present. Furthermore, thermal cycle performance depends on the working temperature range (the highest temperature range, the highest maximum performance coefficient).

Results and discussion

Design and Synthesis

Due to the presence of a hydroxyl group in its structure, which would facilitate its solubility in NH_3 through hydrogen bonds, ammonium ILs related to choline were first considered. However, it is known that an increase on the asymmetry of the cation leads to a reduction on the melting point. For all these reasons, this work was initiated by the synthesis of ILs derived from ammonium incorporating the *N*-ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium cation [EM$_2$NCH$_2$CH$_2$OH] (Figure 1). Besides, considering that adding a second hydroxyl group in the cation would increase the solubility of the IL in NH$_3$, four ILs derived from *N*-ethyl-*N,N*-di-(2-hydroxyethyl)-*N*-methylammonium [EMN(CH$_2$CH$_2$OH)$_2$] were also synthetized.

The design of the ILs was made not only taking into account their expected low toxicity and NH$_3$ solubility, but also their expected thermophysical properties such as melting point, thermal stability and viscosity, which are highly determined by the anion. Due to the suitable properties shown by the ILs derived from bis(trifluoromethanesulfonyl)imide [NTf$_2$][8] and tris(pentafluoroethyl)trifluorophosphate [FAP],[9] these were the first selected anions. However, in order to obtain cheaper ILs, the trifluoromethanesulfonate [OTf] and dicyanamide [DCA] anions, were also selected (Figure 1).

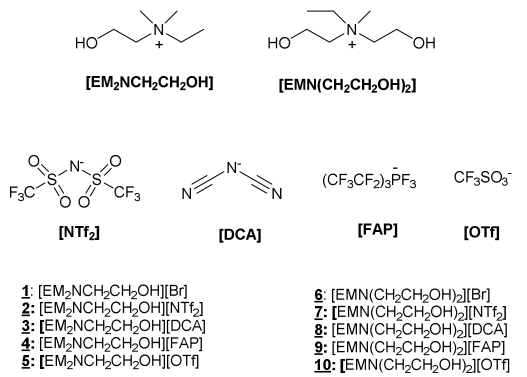
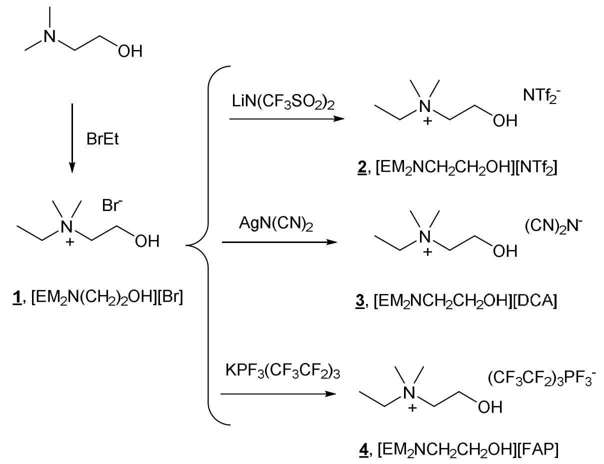


Figure 1 Cations and anions structure of the synthesized salts.

The synthesis of the ILs derived from [EM$_2$NCH$_2$CH$_2$OH] was started by the preparation of *N*-ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethyl ammonium bromide [EM$_2$NCH$_2$CH$_2$OH][Br] (**1**), that was obtained by treatment of *N,N*-dimethylethanolamine with an excess of 1-bromoethane. The subsequent metathesis reactions with the corresponding salts provided [EM$_2$NCH$_2$CH$_2$OH][NTf$_2$] (**2**), [EM$_2$NCH$_2$CH$_2$OH][DCA] (**3**) and [EM$_2$NCH$_2$CH$_2$OH][FAP] (**4**) in high overall yields (Scheme 1)**.**

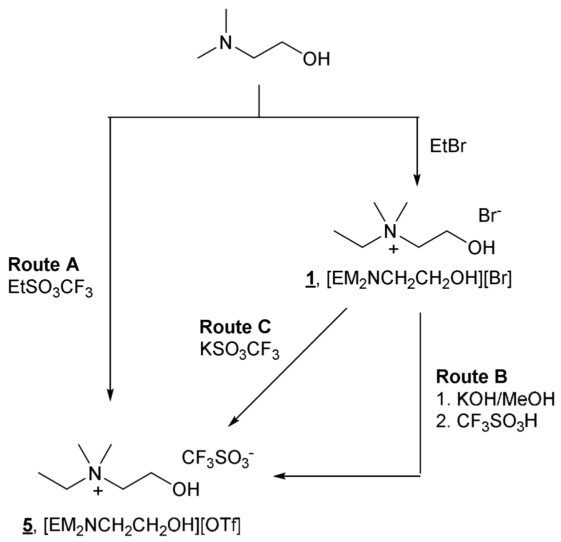
Some problems were found to obtain pure [EM$_2$NCH$_2$CH$_2$OH][DCA] (**3**). Due to its extremely high solubility in water and low solubility in organic solvents, it was not possible to eliminate by precipitation all AgBr salt formed during the metathesis. Furthermore, the IL gave off ammonia odor after some days, even if the IL was kept at room temperature, which indicates decomposition.

The salts [EM$_2$NCH$_2$CH$_2$OH][Br] (**1**) and [EM$_2$NCH$_2$CH$_2$OH][NTf$_2$] (**2**) were already described in the literature[10] but in this work the experimental procedure was optimized. Compounds [EM$_2$NCH$_2$CH$_2$OH][DCA] (**3**), [EM$_2$NCH$_2$CH$_2$OH][FAP] (**4**) and [EM$_2$NCH$_2$CH$_2$OH][OTf] (**5**) are described in this work for the first time.



Scheme 1 Synthetic route for mono-hydroxylated ILs **2-4**.

The synthesis of [EM$_2$NCH$_2$CH$_2$OH][OTf] (**5**) was approached by applying three different routes (Scheme 2). The first route (A) involved a direct quaternization reaction of *N,N*-dimethylethanolamine by treatment with an excess of ethyl trifluoromethanesulfonate to give [EM$_2$NCH$_2$CH$_2$OH][OTf] (**5**) in only one step. However, the presence of a small amount of impurities (≈ 1.5%) was observed in the ^{1}H RMN spectrum of the reaction product. Although different reaction temperatures were tried, it was not possible to obtain [EM$_2$NCH$_2$CH$_2$OH][OTf] (**5**) completely pure by this method. Taking into account the importance of getting very pure ILs, other synthetic approaches were then tried.



Scheme 2 Synthetic routes applied to prepare IL **5**.

The routes B and C consisted in a similar procedure than that applied for ILs **2-4** starting with a quaternization reaction to afford [EM$_2$NCH$_2$CH$_2$OH][Br] (**1**), followed by metathesis. In route B the desired [OTf] anion was incorporated by a first anion exchange to introduce a hydroxyl anion and later neutralization with trifluoromethanesulfonic acid. While in route C the desired [OTf] was introduced by a direct anion exchange of the bromide by treatment with potassium triflate salt. Because its high solubility in water, some problems were also found to obtain pure [$EM_2NCH_2CH_2OH$][OTf] (**5**) when applying B and C routes. The undesired KBr formed during the methatesis reactions was difficult to eliminate. All routes afforded similar high yields, but route C needed less reaction time and only one step.

The structures of all synthetized compounds were confirmed by ^1H, ^{13}C and ^{19}F NMR spectroscopy as well as low and high MS spectrometry (ESI†).

Due to the quadrupole moment of the ^{14}N nucleus, interesting ^1H-^{14}N and ^{13}C-^{14}N couplings[11] were observed in the NMR spectra (Figure 2). Slow quadrupolar relaxation of the ^{14}N nucleus in some tetraalkylammonium salts, makes possible the observation of $J^{14}_{N\text{-}H}$.[12] These couplings appear very clearly in the ^1H NMR spectrum of [$EM_2NCH_2CH_2OH$][DCA] (**3**). Thus, the signal corresponding to the CH_3 of the ethyl group appears as a triplet of triplets due to the coupling with ^{14}N and the neighbour CH_2. On the other hand, the methylenic protons located in α to the N in the 2-hydroxyethyl chain, appear as a characteristic multiplet because of the coupling with the neighbour β-CH_2. Protons α-CH_2 and β-CH_2 give rise an AA'XX' system. According to literature,[13] the characteristic form of this multiplet indicates that the conformation of the cation at room temperature is preferentially *anti* in all synthesized ILs.

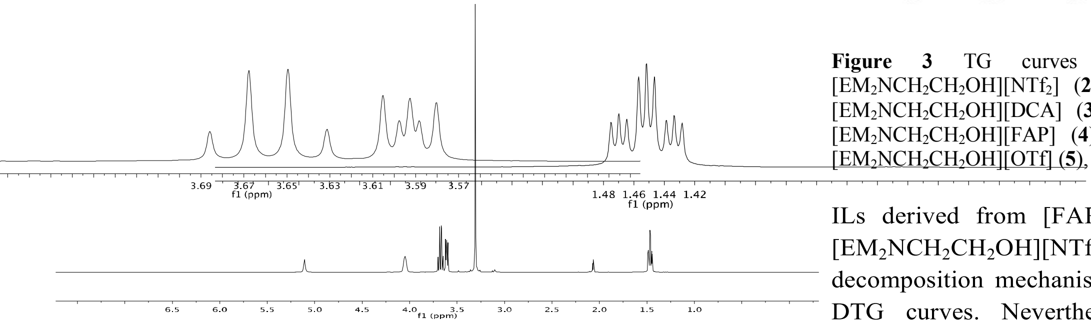


Figure 2 Characteristic multiplets observed in [$EM_2N(CH_2CH_2OH)$][DCA] (**3**) ^1H NMR spectrum due to ^1H-^{14}N couplings.

The synthetic route applied to prepare the di-hydroxylated salts [$EMN(CH_2CH_2OH)_2$][Br] (**6**), [$EMN(CH_2CH_2OH)_2$][NTf_2] (**7**), [$EMN(CH_2CH_2OH)_2$][DCA] (**8**) and [$EMN(CH_2CH_2OH)_2$][FAP] (**9**) was the same than that employed for salts **1-4** but starting from *N,N*-di-(2-hydroxyethyl)-*N*-methylamine instead of *N,N*-dimethylethanolamine. However, due their higher solubility in water, different procedures were used for their isolation.

In the case of [$EMN(CH_2CH_2OH)_2$][OTf] (**10**), the route C previously applied to prepare for [$EMN(CH_2CH_2OH)_2$][OTf] (**5**), was selected.

Because their high solubility in water, problems were also found to purify [$EMN(CH_2CH_2OH)_2$][NTf_2] (**7**) and [$EMN(CH_2CH_2OH)_2$][OTf] (**10**). LiBr and KBr salts formed during the methathesis reactions were very difficult to eliminate. Most of them were eliminated by precipitation, but later application of Solid Phase Extraction methodology was needed to remove the small amount of still remaining inorganic salts.[c] As it was expected, ^1H-^{14}N and ^{13}C-^{14}N couplings in the ^1H NMR spectra similar to those of mono-hydroxylated ILs **1-5**, were observed.

Thermal stability

Figure 3 shows the TG curves of the eight ILs. The different forms suggest distinct mechanisms of decomposition. This fact is clearly exposed in Figure S1 (ESI†), where both TG and DTG curves are shown. The onset and endset temperatures, mass remaining at onset and 600 ºC and temperature corresponding to 10% of mass loss obtained from the TG curves, as well as the peak temperatures determined from the DTG curves are shown in Table 1.

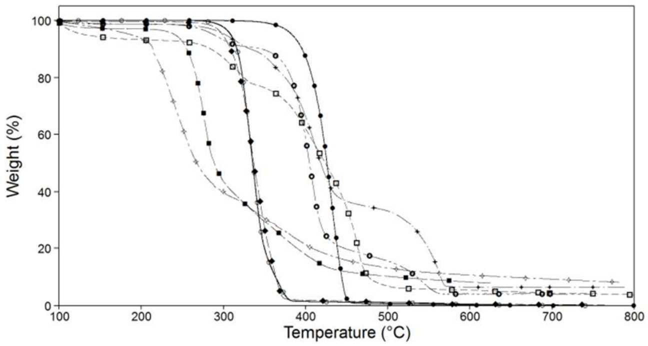


Figure 3 TG curves of the eight synthesized IL (●) [$EM_2NCH_2CH_2OH$][NTf_2] (**2**), (□) [$EMN(CH_2CH_2OH)_2$][NTf_2] (**7**), (■) [$EM_2NCH_2CH_2OH$][DCA] (**3**), (✧) [$EMN(CH_2CH_2OH)_2$][DCA] (**8**), (♦) [$EM_2NCH_2CH_2OH$][FAP] (**4**), (☼) [$EMN(CH_2CH_2OH)_2$][FAP] (**9**), (✦) [$EM_2NCH_2CH_2OH$][OTf] (**5**), (◉) [$EMN(CH_2CH_2OH)_2$][OTf] (**10**).

ILs derived from [FAP] and [DCA] anions together with [$EM_2NCH_2CH_2OH$][NTf_2] (**2**), mainly showed a single decomposition mechanism characterized by one peak in their DTG curves. Nevertheless important differences can be observed between them; [$EM_2NCH_2CH_2OH$][NTf_2] (**2**) showed the greatest global mass change (0.2% remaining at 600 ºC) and the narrowest temperature degradation interval ($\Delta T = T_{endset} - T_{onset}$) 40 ºC, also showed in Table 1. Similar behaviors can be observed in ILs incorporating [FAP] anion, although some shoulders appeared in the second part of the DTG curves.

A slowly slope change on the last part (after 300 ºC) of the TG curve of the ILs with [DCA] anion suggests a change on the decomposition mechanism, which could be due to the presence of impurities in the sample. Shamsipur et al.[14] and Salgado et al.[15] found similar behaviors in the dynamic TG curves of imidazolium and pyrrolidinium based ILs, being necessary more than 800 ºC to eliminate completely the sample. These results are in agreement with the problems found during their preparation above mentioned.

Table 1 Onset and endset temperatures (T_{onset}, T_{endset}), DTG peak temperatures (T_{peak1}, T_{peak2}, T_{peak3}), mass remaining at onset (W_{onset}), mass remaining at 600 ºC (W_{600}) and temperature corresponding to 10% of mass loss ($T_{10\%}$) for all ILs synthesized. Temperatures are given in ºC.

Ionic Liquid	T_{onset}	W_{onset} (%)	T_{endset}	ΔT	T_{peak1}	T_{peak2}	T_{peak3}	W_{600} (%)	$T_{10\%}$
[$EM_2NCH_2CH_2OH$][NTf_2]	406	82	446	40	432			0.2	396
[$EMN(CH_2CH_2OH)_2$][NTf_2]	375	72	477	198	323	463		5.4	285
[$EM_2NCH_2CH_2OH$][OTF]	348	87	569	280	316	412	562	6.5	333
[$EMN(CH_2CH_2OH)_2$][OTF]	383	80	558	291	295	405	542	4.1	355
[$EM_2NCH_2CH_2OH$][FAP]	316	90	379	63	336	369		0.5	316
[$EMN(CH_2CH_2OH)_2$][FAP]	312	87	370	58	332	345	360	0.5	309
[$EM_2NCH_2CH_2OH$][DCA]	258	88	423	165	276			8.0	256
[$EMN(CH_2CH_2OH)_2$][DCA]	212	91	440	228	240			11	214

TG curves corresponding to the ILs incorporating [OTf] anion are more complex because they exhibit three decomposition degradation steps. Thus, broader temperature intervals to complete the thermal degradation are observed in these cases. The first degradation step detected for these ILs (onset temperatures at 289 ºC and 267 ºC, for [$EM_2NCH_2CH_2OH$] and [$EMN(CH_2CH_2OH)_2$] respectively) could be attributed to the loss of tied water, which is difficult to eliminate even drying under vacuum. To confirm the origin of this first step, a series of three experiments combining isothermal and dynamic scans were performed. The procedure consisted in carrying out an isothermal scan at 260 ºC (lowest onset temperature for this peak in the ILs studied), for a given time of exposition (15 min, 30 min or 60 min), followed by cooling to 150 ºC and a later dynamic scan heating up to 800 ºC at 10 ºC/min. Figure 4 shows the TG curves of these three experiments with regard to time (a) and sample temperature (b). As it can be observed in figure S1c, the TG curve without preheating at 260 ºC shows three separated steps, and the first one at 289 ºC involves a loss of 9% of initial weight. However, figure 5a shows that 15 min of preheating at 260 ºC reduces significantly the weight loss of this peak up to 5% approximately, while preheating for 30 min and 60 min implies a total reduction of this step.

On the other hand, no differences neither on temperature nor weight loss can be observed on the second step (at 348ºC) with the previous preheating in any case. These facts corroborate the hypothesis on which the origin of the first process of mass loss was due to the presence of tied water, being necessary to heat at 260 ºC for 30 min to eliminate it. On having expelled this tied water, an increase in preheating time does not cause a visible effect on the degradation curve, which indicates that IL degradation did not start at this temperature.

Determining the thermal stability from the dynamic analysis, the anion trend obtained for this selection of ILs is [NTf_2] > [OTf] > [FAP] > [DCA]. In spite of the fact that no data of these ILs properties could be found, and taking into account that the anion effect is higher than that of the cation, this trend agrees with the results described in literature. However, the values obtained in this work for ammonium ILs are slightly lower than those of imidazolium, phosphonium or pyrrolidinium based ILs incorporating similar anions.[15-17] On the other hand, based in these results from the dynamic TG scans, thermal stability seems to be relatively higher for monohydroxylated ILs with [$EM_2NCH_2CH_2OH$] cation than for those di-hydroxylated with [$EMN(CH_2CH_2OH)_2$] cation, although differences in [FAP] based ILs are not as significant as those observed for the other studied anions.

With the aim to determine the long-term thermal stability and the maximum operation temperature, the four ILs with the highest T_{onset} were selected to perform several isothermal experiments at different temperatures. The corresponding TG scans are shown in Figure 5.

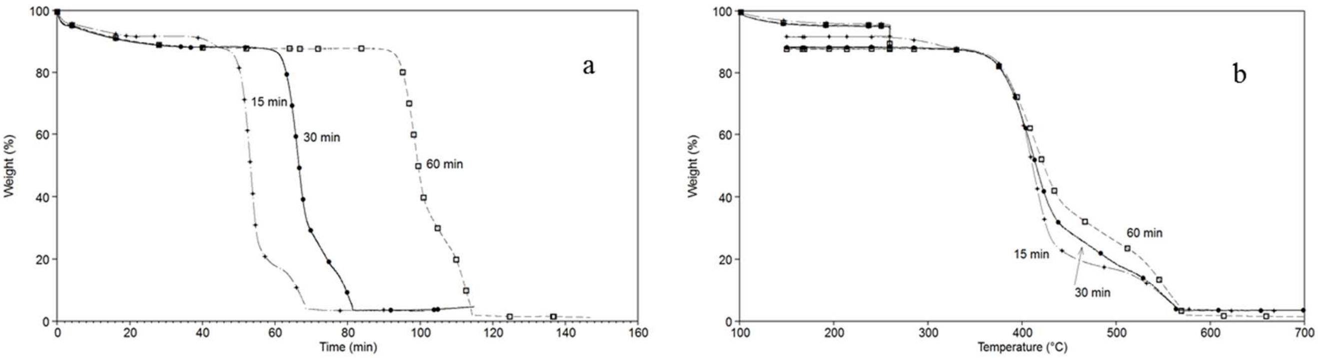


Figure 4 TG curves of combination of isothermal scans at 260 ºC for different times with dynamic scans for [$EM_2NCH_2CH_2OH$][OTf] (**10**) against time (a) and sample temperature (b).

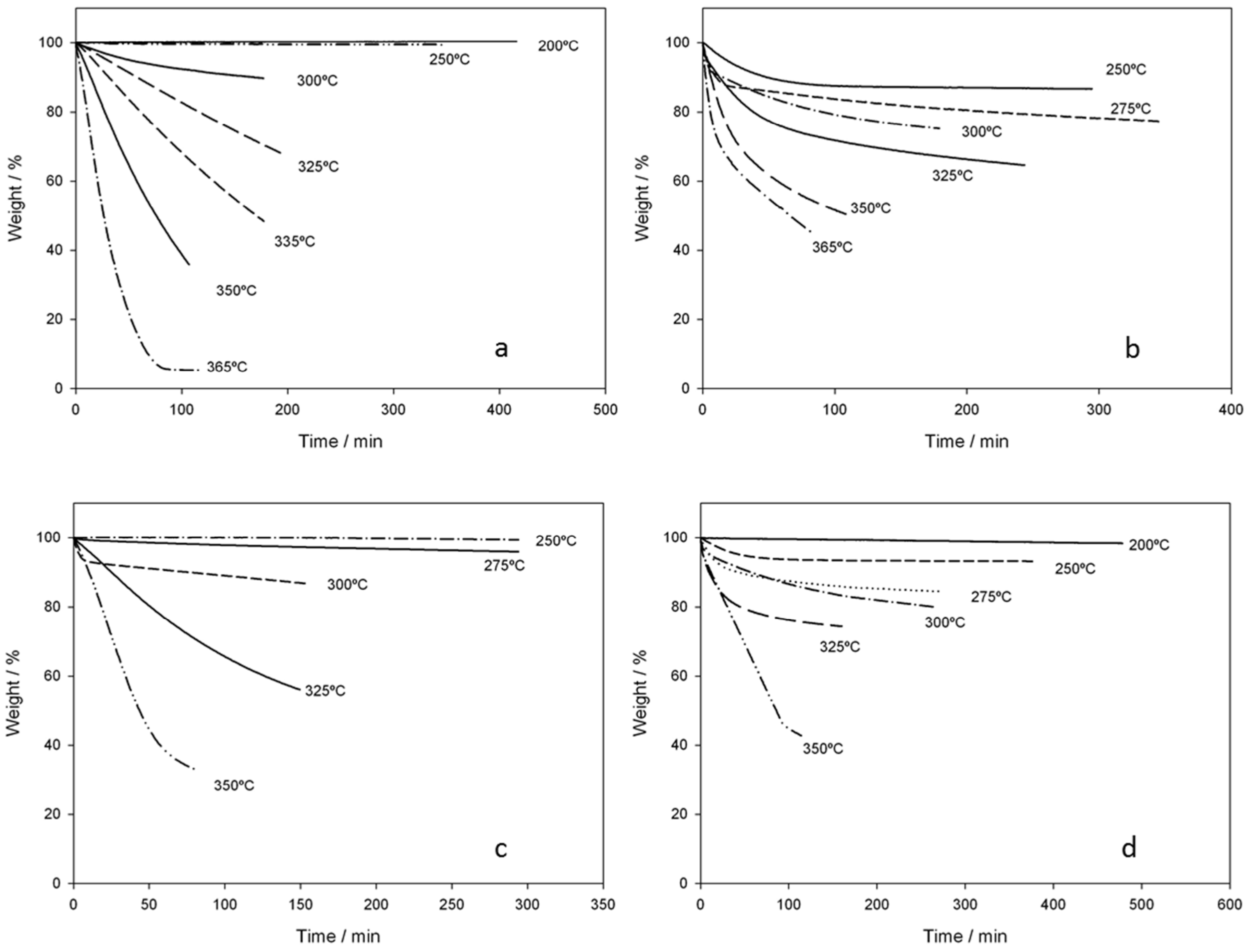


Figure 5 Isothermal scans at different temperatures for the ILs: (a) [$EM_2NCH_2CH_2OH$][NTf_2], (**b**) [$EMN(CH_2CH_2OH)_2$][NTf_2], (c) [$EM_2NCH_2CH_2OH$][OTf] and (d) [$EMN(CH_2CH_2OH)_2$][OTf].

The long-term thermal stability shows a similar trend than that indicated from the temperature ramped studies, but ILs degrade at significantly lower temperatures than onset temperature. As it was expected, the isothermal TG curves at the highest temperatures are characterized by a fast degradation in all cases; by the contrary, a thermal degradation is hardly appreciable in the TG scans during more than 5 hours at 200 ºC and 250 ºC.

It is important to note the different behaviour observed for the lowest temperatures scans and the highest. All the isothermal scans at temperatures less than 250 ºC show a linear decay, with a small slope and without initial loss of mass. However, scans to temperatures higher than 250 ºC-300 ºC present an important loss during the first 30 min approximately followed by an almost lineal mass loss, except for [$EM_2NCH_2CH_2OH$][NTf_2] (**2**). These observations agree with the possible loss of tied water as it was mentioned above.

Following the Wooster criteria[19] that choose as a good indicator of thermal stability the temperature at which 1% degradation occurs in 10 h, the long-term stability of these ILs is 200 ºC.

Degradation kinetics

The kinetics of decomposition of ionic liquids with the anions [NTf_2] and [OTf] was analysed from isothermal TG results following the methodology reported in a previous paper.[16]

The temperature dependence on the rate of loss mass, k, is represented by the Arrhenius equation:

$$k = A\exp\left(\frac{-E_a}{RT}\right) \qquad (1)$$

where E_a is the activation energy and A is the pre-exponential coefficient. Figure 6 shows the relation between the values of ln k and T^{-1}. Thus, from the corresponding linear fitting, the activation energy of the degradation process has been obtained, and showed in Table 2.

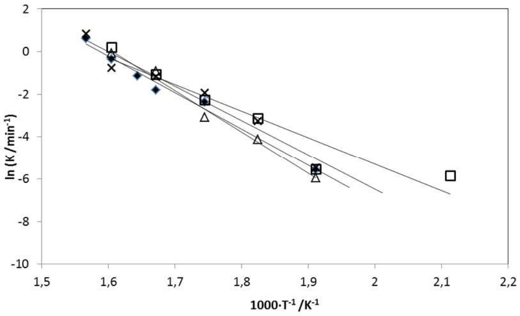


Figure 6 Arrhenius plots for the four ILs (♦) [$EM_2NCH_2CH_2OH$][NTf_2], (x) [$EMN(CH_2CH_2OH)_2$][NTf_2], (Δ) [$EM_2NCH_2CH_2OH$][OTf], (□) [$EMN(CH_2CH_2OH)_2$][OTf]

Up to now no references with values of this parameter for these ILs were found, although these values are in concordance with those reported in the literature for other ILs.[7,15,16,20-24]

Activation energy of ILs with the anion [NTf_2] are the lowest, agreeing with previous results of Salgado et al.[15,16] On the other hand, although differences between the cations are small, these results show that the activation energy of monohydroxylated ILs is a little bit higher than the corresponding to those dihydroxylated for both anions.

From the comparison between the results obtained in our laboratory and those published in previous papers, it can be concluded that activation energy presents the follow trend: imidazolium < hydroxylated ammonium < pyrrolidinium ILs with the same anion.

Table 2 Activation energy of thermal degradation process for selected ILs.

IL	E_a (kJ/mol)
[$EM_2NCH_2CH_2OH$][NTf_2]	140 ± 10
[[$EM_2NCH_2CH_2OH$]][NTf_2]	135 ± 15
[$EM_2NCH_2CH_2OH$][OTf]	160 ± 15
[[$EM_2NCH_2CH_2OH$]][OTf]	140 ± 10

Experimental

Thermal stability

A thermogravimetric analyzer (TGA 7 - Perkin Elmer), operating in dynamic and isothermal modes under dry air atmosphere, was used to perform thermogravimetric analysis.[16] Liquid samples of (4 ± 1) mg were placed in an open platinum pan. Dynamic experiments were performed at temperatures from (100 to 800) ºC, with a heating rate of 10 ºC min^{-1} and a purge gas flow of 20 $cm^3 min^{-1}$.

Using the thermal analysis software, onset temperatures (T_{onset}) were calculated by the intersection of the straight baseline along the temperature axis from a low temperature region where there is no weight loss, and a straight line created through the inflection point (previously determined as a minimum in the derivative of the mass loss curve, DTG) of the mass versus temperature data.[16,20] From these curves, remaining mass at onset point, remaining mass at 600 ºC, temperatures for minima of the DTG peaks and temperatures for the 10% of the initial mass were also determined. Each analysis was repeated three times, the standard deviation average values being lower than 6 ºC in all the cases.

On the other hand, isothermal TG analysis was used to determine the long-term thermal stability of the four ILs with the highest T_{onset}. This analysis provides rates of decomposition at a given temperature after a given isothermal-heating time. Several temperatures in the interval (200 ºC - T_{onset}) were selected for these scans. Taking into account that at 200 ºC the mass loss was lower than 1% in 5 hours for the studied ILs, experiments at temperatures lower than 200 ºC were not performed. From these experiments the kinetics of decomposition were analyzed and the maximum operation temperatures of these ILs were estimated following the methodology reported in previous papers.[15,16,20]

Conclusions

Two series of ammonium ILs related to choline derived from *N*-ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium and *N*-ethyl-*N,N*-di-(2-hydroxyethyl)-*N*-methylammonium cations incorporating different anions, were designed to be applied as potential absorbents in working pairs with NH_3. Their synthesis was carried out by a quaternization reaction of the suitable amine followed by methatesis. Their structures were confirmed by ^{1}H, ^{13}C and ^{19}F NMR spectra as well as low and high Mass Spectrometry. Eight of the prepared ILs are described in this work for the first time.

The ILs NMR spectra showed the presence of characteristic multiplets due ^{1}H-^{14}N and ^{13}C-^{14}N couplings. The analysis of these multiplets indicates that the conformation of the cation at room temperature is preferentially *anti* in all synthesized ILs.

Thermogravimetric studies revealed that the anion influence on the thermal stability is higher than that of the cation. The onset temperatures, measured in dynamic conditions, showed that the anion influence follows the trend: $[NTf_2]$ > [OTf] > [FAP] > [DCA]. Related to the cation effect, it has been found that the monohydroxylated cation *N*-ethyl-*N*-(2-hydroxyethyl)-*N,N*-dimethylammonium presents slight higher thermal stability than the dihydroxylated *N*-ethyl-*N,N*-di-(2-hydroxyethyl)-*N*-methylammonium.

Isothermal analysis at temperatures 20 ºC below the onset temperature showed a fast degradation. TG scans at 200 ºC revealed a hardly appreciable degradation after 10 hours.

Activation energy of degradation process, determined from Arrhenius equation, follows the sequence imidazolium < hydroxylated ammonium < pyrrolidinium ILs with the same anion. Besides, the sequence observed with regard of the anion is: $[NTf_2]$ < [OTf] for imidazolium, pyrrolidinium and hrydroxylated ammonium ILs.

From the thermal analysis of the ILs synthesized, it can be concluded that some of them would be suitable to be applied as potential absorbents in working pairs with ammonia. Studies on their NH_3 solubility and other physical properties are under current research.

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Notes and references

[a] Department of Organic Chemistry, University of Vigo, Marcosende, Vigo, Spain.
[b] Department of Applied Physics, Thermophysical Properties of fluids and biomaterials, University of Santiago de Compostela, Santiago de Compostela, Spain

[c] The optimization of Solid Phase Extraction methodology applied to ionic liquids purification is under current research.

*E-mail: etojo@uvigo.es

† Electronic Supplementary Information (ESI) available: [synthetic procedures, ^{1}H, ^{13}C, ^{19}F NMR, MS data]. See DOI: 10.1039/b000000x/

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