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Thermal Behaviour of Pure Ionic Liquids

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1. Introduction

The interest in ionic liquids (ILs) that has developed during in the past few decades is well-recognized. This interest has developed mainly due to their special properties such as high thermal stability, high electrical conductivity, high heat capacity per unit volume, wide temperature range in a liquid state, good solvent properties and especially their negligible vapour pressure, which render them popular compounds. This popularity is reflected in the great deal of publications that relate the potential applications of ILs in different fields, among which can be highlighted their use as solvents, electrochemical applications and more recently, as heat transfer fluids.

In order to use the ILs at an industrial scale, deep knowledge of their thermophysical properties is vital, since these properties not only determine the equipment size needed, but also directly influence its design parameters; for example, melting and glass transition temperatures are needed to set a feasible temperature operation range and heat capacity is essential for estimating the heat exchange in unit operations, as well as heat storage capacity. Moreover, knowledge of these thermophysical properties, such as freezing, melting, cold crystallization, glass transition temperatures and heat capacities, allows for better understanding the stabilities and structures of these relatively new compounds.

In the extensive literature dealing with thermophysical properties of pure ILs, different authors have applied various methodologies and equipment for the study of the thermal behaviour of ILs and for the determination of their heat capacities. This has led to discovering discrepancies in these literature values. For this reason, special attention must be paid to experimental procedures and to the different factors affecting the determination of these properties. Recently, differential scanning calorimetry (DSC) has been widely used for the determination of these properties due to its simplicity and because only a small sample is required. For all of

the above-mentioned factors, a suitable working protocol for the correct determination of phase transition temperatures and heat capacities using DSC will be described in this chapter.

Nowadays, there are enough experimental data available in the literature concerning the thermal analysis and heat capacities of pure ionic liquids, which allows for drawing general conclusions about the influence of the structure of ionic liquids on these thermophysical properties. As such, the main behaviours of ionic liquids as found in the literature will be described and analysed in this chapter, together with the influence of the structures of the ionic liquids (cation, anion and alkyl-side chains of the cation) on their heat capacities.

In addition, different methods for the estimation of melting and glass transition temperatures, as well as heat capacities can be found in the literature; the basis of these methods, as well as some applications for estimating the thermal properties of IL will be presented. The extension of the selected database for these methods and their average deviation will be compared.

2. Thermal analysis

Thermal analysis allows for establishing the behaviour of a material when it is heated or cooled. The structure of a material undergoes changes such as melting and freezing when it is subjected to changes in temperature. In the case of ionic liquids, this process is necessary not only because most ionic liquids are new substances and therefore have unknown properties, but also because their applicability is conditioned to their liquid state.

Regarding the interpretation of the thermal analyses, in this chapter, melting temperature (Tm) was taken as the onset of an endothermic peak (downward deflection of the curve peak) upon heating, freezing temperature (Tf) as the onset of an exothermic peak (upward deflection of the curve peak) upon cooling, cold crystallization temperature (Tcc) as the onset of an exothermic peak upon heating from a subcooled liquid state to a crystalline solid state, solid-solid transition (Tss) as the onset of an exothermic or endothermic peak upon heating from a crystalline solid state and glass transition temperature (Tg) as the midpoint of a small heat capacity change upon heating from the amorphous glass state to a liquid state.

2.1. Methodology

Although thermal analysis is a widely known technique applied for studying the thermal behaviour of substances, there are several factors that affect the determination of transition temperatures. Among these, the most important are sample size, the thermal history of the sample and the cooling and heating rate of the scan. Nowadays, the most used technique for the thermal analysis of pure ionic liquids is differential scanning calorimetry (DSC). Hence, in this section, an adequate work methodology using DSC is described as attending to all of the above-mentioned factors in an attempt to standardize the thermal analysis determination. Standardization of the work methodology is important for comparing data obtained from different authors, since the research studies available in the existing literature do not always state their applied methods in detail. Below, the suggested work methodology is described:

i. Sample preparation.

a. **Sample amount**. The sample amount recommended for a study on phase transitions is approximately 4-8 mg, since the sample amount is directly related to the peak size (the greater the sample size the greater the signal); however, the resolution will be lower and overlapped effects may appear. For this reason, for the determination of transition temperatures, it is recommended that a small sample size is used.

b. **Weighing**. Considering that the sample weight is directly related to the accuracy of the measurement, it is vital to use a balance with a precision of at least ± 0.00001 g. Additionally, since the DSC technique uses a reference crucible, it is advisable that the mass of both crucibles (sample and reference) is as similar as possible.

c. **Crucibles**. Most of the thermal transitions are perfectly determined with a standard aluminium crucible. With this technique, it is possible to work with the crucible open (without lid) or to have it hermetically sealed. It is recommended that hermetically sealed crucibles be used, because in this way, heat flow caused by evaporation is avoided and radiation emitted by the sealed sample and reference crucible, are similar. In addition, when working with sealed crucibles there is the possibility of making a pinhole in the lid to avoid a pressure increase inside the crucible.

d. **Sample placement**. Besides the usual conditions applied in any experimental measurement, careful attention should be paid to sample placement, which should be done in a manner that facilitates good contact between the sample and the crucible bottom.

ii. Method.

a. **Dry step**. Due to the known influence of the water amount and impurities present in the properties of ILs, it is necessary to subject the simple to a previous drying step. Therefore, the sample should be heated at a temperature high enough to evaporate water and impurities; for instance, a suggested dry step will be to maintain the sample at $T = 120°C$ for 30 minutes inside the furnace. A good way to know the dryness degree of the sample is to weigh the sample before and after the dry step.

b. **Thermal history**. Various materials present different thermal effects, depending on their thermal history; this thermal history can be eliminated by subjecting the sample to a previous heating. For this reason, the working protocol must begin with a heating of the sample to eliminate its thermal history which could lead to incorrect results. Note that if the dry step is carried out inside the furnace of the DSC, the thermal history of the ionic liquid will be eliminated.

c. **Heating and cooling rate**. This is the most important factor in any thermal analysis, as crystallization transitions strongly depend on the cooling and heating rate (low rates can give the ionic liquid time enough to form crystals).

Due to the special nature of ionic liquids, variations upon heating and cooling rates are useful for studying their thermal transitions. Taking into account that at fast rates the phase transition peaks can appear overlapped, while at slow rates these peaks can move apart from each other, a recommended practice is to begin the study of a sample by a scan carried out at a relatively slow heating rate of 2°C/min to gain better information about the thermal behaviour of the sample, including whether the ionic liquid is a crystal or a glass former, the presence of polymorphs, etc.

Taking into account all of the above-mentioned factors, the proposed work methodology for the thermal analysis of pure ionic liquid is explained below.

1. **Dry step.**

2. **First cooling and heating cycle**. The thermal analyses start with a "slow method" consisting of a cooling cycle from 120°C to -140°C, followed by a heating cycle from -140°C to 120°C at 2°C/min. The chosen start and end temperatures are 120°C and -140°C, respectively, because the usual behaviour of ionic liquids shows that in case the IL presents a glass transition, this transition will appear at low temperatures and the ILs will not present transitions above 120°C. It is important for the correct characterization of the thermal behaviour of ILs to reach temperatures low enough to observe the possible apparition of a glass transition. This is why, in the literature, many studies remain incomplete, because in their temperature range the cooling cycle began at room temperature and the heating cycle also ends at room temperature.

3. **Complementary cycles**. Depending on the transitions appearing in the first cooling and heating cycle, for a complete and correct characterization of the sample, other heating and cooling cycles should be carried out. If only a Tg appears in the slow method, the study of the thermal behaviour of this IL is completed and it can be concluded that the studied ionic liquid shows a strong tendency for forming glass. However, if the slow method shows that the ionic liquid presents any other transition but does not present a glass transition, the sample is subjected to a faster cooling or quenching to avoid crystallization. This cooling can be performed in different ways: by cooling the sample from 120°C to -140°C at 40°C/min, followed by a heating cycle, or by introducing the sample into liquid nitrogen to achieve rapid fast cooling. The problem lies in the scans where the association between peaks and phase transition is not clear. At this point, a customized protocol should be proposed.

4. **Study of polymorphic behaviours**. Following on, an approach to the study of an ionic liquid presenting polymorphic behaviour will be discussed with the help of Figure 1. As can be observed, this IL did not form crystals upon cooling at 2°C/min, while upon heating, the IL presented a Tg and Tcc at -90°C and -70°C, respectively. These two transitions were easily assigned; the peaks with difficult interpretation were those placed between -35°C and -20°C, which is typical in polymorphic compounds. The peak appearing at -35°C is an endothermic transition; however, it is unclear whether this peak represents a solid-solid or a melting transition. The next peak (which are actually two peaks overlapped)

may have been caused by the melting of different crystals or by a solid-solid transition followed by a melting, or by a melting followed by a recrystallization, which immediately melted. In order to assign with certain reliability these peaks to their corresponding transitions, further experimentation has to be conducted. To answer the first question, a run with a different heating rate that aims to determine whether this peak disappears or moves will be useful; in case it moves, the melting transition is not probable and it can be stated that represents a solid-solid transition (in general, the formation of a metastable crystal). Once confirmed that the first peak corresponds to a solid-solid transition, the second peak can be more easily interpreted. This peak can be associated with the melting of the metastable crystal, which occurs with the recrystallization of a stable crystal that finally melts. In cases like this example, if further cooling and heating rates do not yield better information, it will be necessary to use techniques such as X-ray diffraction. This example shows the importance of subjecting the IL to different heating and cooling rates in order to interpret the thermograms.
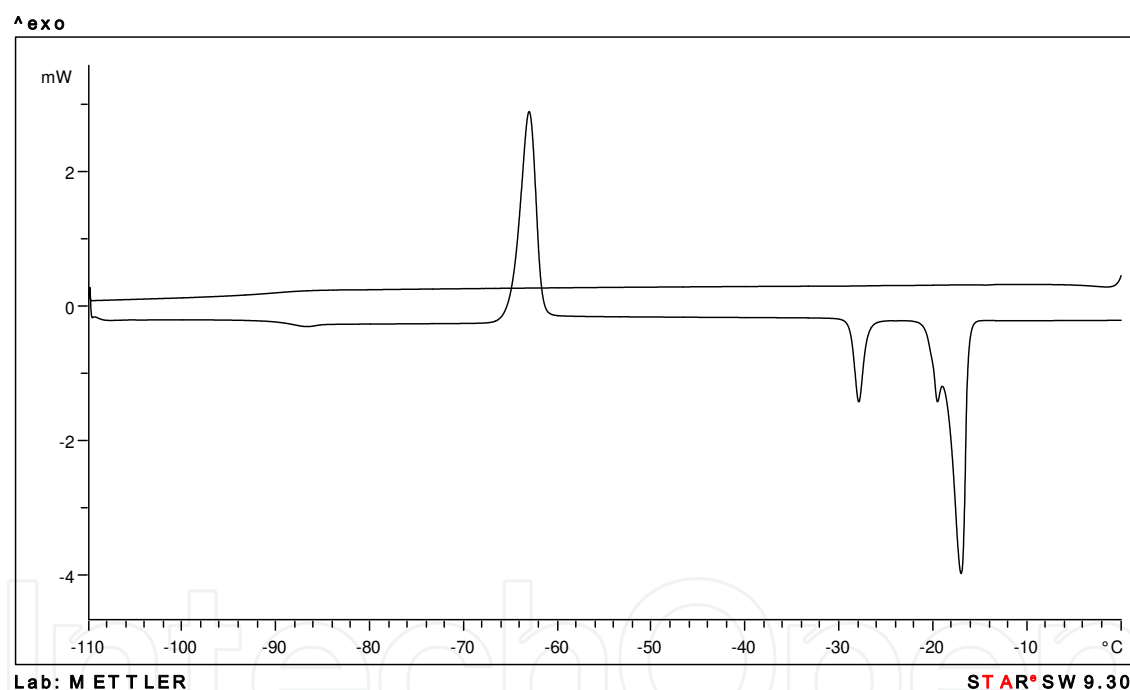

Figure 1. Thermogram of the ionic liquid BMpyrNTf$_2$ cooling from 120°C to -140°C, followed by heating from -140°C to 120°C at 2°C/min.

It is remarkable that in this example, there was only one solid-solid transition (endothermic), but it is usual in polymorphic ionic liquids that several solid-solid transitions, endothermic and/or exothermic, are present, which increases the difficulty of the interpretation of DSC curves.

In Table 1 below, the transition temperatures observed by several authors for the IL BMpyrNTf$_2$ are presented. Here, the disparities within the results taken from literature obtained using different methods for the same IL are reflected.

Ref.	Tg / ºC	Tcc / ºC	Tss / ºC	Tss / ºC	Tm / ºC	Tm / ºC
1	-87[a]	-55		-24	-18	
2	-85[b]	-53		-30	-18	
	-85[b]	-53				-7
3	-92[c]	-69	-47			-11
	-87[c]	-56		-34	-21	
	-87[c]	-56		-34	-21	-11
4						-6
5	-87[d]	-53			-18	

[a] taken as the onset of the transition upon heating

[b] taken as the midpoint of the transition upon heating

[c] not stated

[d] taken as the midpoint of the transition upon cooling

Table 1. Transition temperatures for the IL BMpyrNTf$_2$ obtained by several authors.

MacFarlane et al. [1] determined in their study the phase transitions of the IL BMpyrNTf$_2$ by heating at 10°C/min after quenching from the liquid state; Kunze et al. [2] obtained similar results with a similar method (heating at 10°C/min after quenching at 40°C/min from 40°C to -150°C) and by changing the cooling rate to 2°C/min, determined a Tm = -7°C without detecting a solid-solid transition. The most extensive study on thermal analysis for this ionic liquid was carried out by Stefan et al. [3], who performed three different methods for fully characterizing the IL and found three types of crystals. In the paper published by Kunze et al. [4], the researchers only registered the melting transition by cooling the sample at 20°C/min and heating it at 10°C/min. Finally, Jin et al. [5] reported similar values than those presented in [1] and [2], but did not report the solid-solid transition. The method used by these authors was first a heating cycle to 80°C, followed by a cooling to -150°C at 10°C/min and a final heating cycle to 80°C at 10°C/min. The DSC experimental results shown in Table 1 indicate, as expected, that phase transitions were dependent on the scanning rate and on the cooling method used to obtain the solid phase (quenching or slow cooling).

Finally, it is not always possible to correctly identify the different transitions appearing in a thermogram of a polymorphic ionic liquid using DSC. The techniques that can be used to achieve a clear interpretation are those attached to the DSC, such as crossed polarizing filters or a microscope, as well as techniques that are carried out separately such as X-ray diffraction and infrared spectrometry.

2.2. Types of thermal behaviours of ILs

In this part of the chapter, the main types of thermal behaviours found for ILs are described. In general, in the literature [6-10], these behaviours are divided into three groups:

i.   The first type of behaviour is formed by ionic liquids characterized by presenting only the formation of amorphous glass.

ii. The second type of behaviour is characterized by presenting a freezing transition, forming crystals upon cooling and a melting transition upon heating.

iii. The third type of behaviour that appears in ILs does not show a tendency to crystallize upon cooling; however, upon heating, cold crystallization is exhibited.

The thermal behaviour of ILs is not directly related to their structure; for this reason, some examples of ILs presenting each of the three thermal behaviours above will be presented, in a way to explain how ionic liquids with different structures present the same behaviour and ionic liquid with similar structures present different behaviours.

i. As mentioned above, the first type of behaviour is characterized by no true phase transitions, but only the formation of an amorphous glass. The ILs included in this type do not have melting or freezing points, only glass transition temperatures. These ILs are good glassy-formers, which indicates that they present a weak tendency for crystallization. Several examples of ILs presenting this behaviour can be found in the literature, among them $BMimBF_4$ [10], $BMMimPF_6$ [10], $C_3CNMimDCA$ [8], $BMpyNTf_2$ [6], $EMpyESO_4$ [6], $BMpyBr$ [6], $PMimNTf_2$ [11], $HMimDCA$ [11] and $PMpyNTf_2$ [12]. Taking into account that the glass transitions of ILs usually appear at low temperatures, it is important to work at temperatures as low as -120°C. The glass transition appears both in the cooling and in the heating cycles; when a glass transition temperature for an IL is given, the cycle where it is observed (cooling or heating) must be specified. Figure 2 shows a thermogram for $PMpyNTf_2$ at a cooling and heating rate of 10°C/min; this IL is characterized by the presence of only a glass transition. In the following section, the influence of the cooling and heating rate on this phase transition temperature will be discussed.
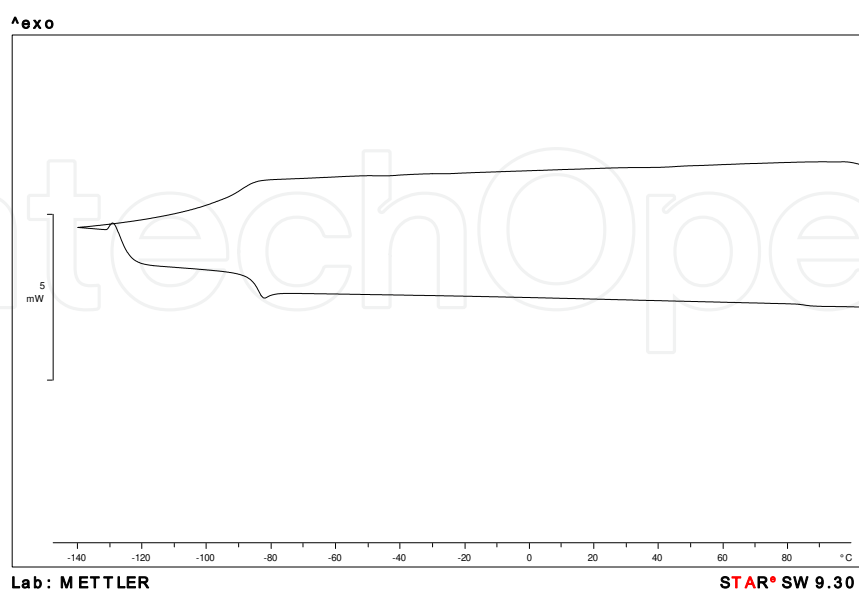

Figure 2. Thermogram of the ionic liquid $PMpyNTf_2$ [12] cooling from 120°C to -140°C, followed by heating from -140°C to 120°C at 10°C/min.

ii.   The ILs presenting a freezing transition upon cooling and a melting transition upon heating belong to the second type of behaviour. These ILs present a strong tendency for forming crystals. However, there are ILs that in other cooling conditions will undergo a glass transition. To test their tendency to form crystals, these ILs should be subjected to a faster cooling rate to avoid crystallization; this methodology was adopted for the present study, as was indicated in the previous section. Generally, in these ILs freezing temperatures are markedly lower than melting temperatures, an effect known as supercooling. The ILs $EMimNTf_2$ [11], BMpyTFO [12], BMimTFO [12], $EMpyNTf_2$ [12], HMimTFO [11], $EMMimNTf_2$ [10], $C3CNTMANTf_2$ [8] and BpyBr [6] are examples of ILs presenting this behaviour. In Figure 3, a typical thermogram for this type of behaviour is presented.
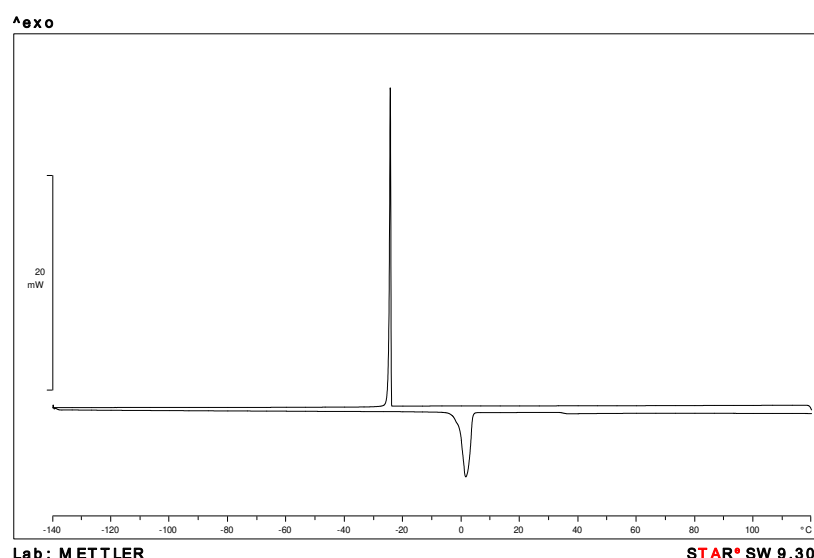

Figure 3. Thermogram of the ionic liquid $EMpyNTf_2$ [12] cooling from 120°C to -140°C, followed by heating from -140°C to 120°C at 2°C/min.

iii.   The ILs that do not form crystals upon cooling, but present a glass transition at low temperatures and upon heating, and that first suffer a glass transition followed by a cold crystallization to finally melt, are included in the third type of behaviour. The subcooling phenomenon (cold crystallization) is usually associated with polymers and other amorphous materials, and is present in the thermal behaviour of many ionic liquids. Among the ILs belonging to this group are $BMimNTf_2$ [11], $HMimNTf_2$ [11], BMimDCA [10,12], $EMimNTf_2$ [10], $BMimPF_6$ [10], $BMMimBF_4$ [10], $HpyNTf_2$ [6] and $C3CNMMimPF_6$ [8]. In Figure 4 below, the typical scan for this third behaviour is illustrated.

Note that the three behaviours explained above are the simplest behaviours that can be found in the study of ionic liquids, since the polymorphism phenomenon can be found on ILs included in the second and third groups. This phenomenon deserves careful attention, because the association between peaks and transitions is not always clear. It is noteworthy that an IL
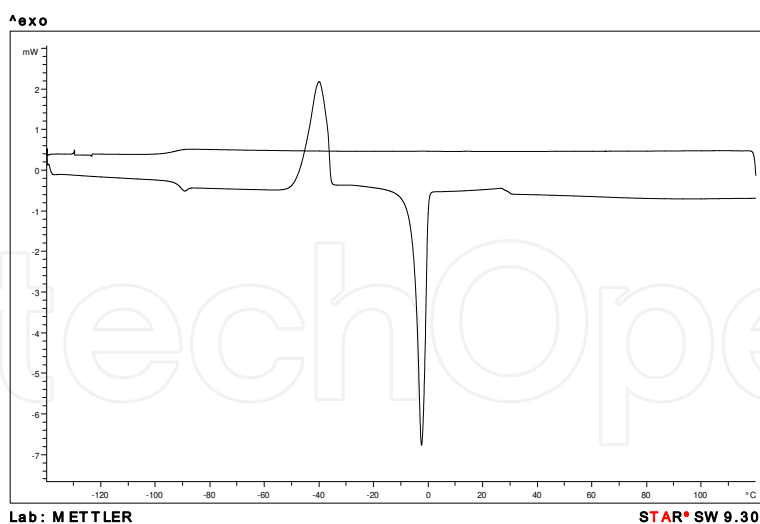
Figure 4. Thermogram of the ionic liquid BMimDCA [12] cooling from 120°C to -140°C, followed by heating from -140°C to 120°C at 2°C/min.

belonging to a certain group and subjected to different conditions can become part of a different group. Figure 5 below illustrates how the ionic liquid BMpyTFO, belonging to the second group, when subjected to a cooling and heating rate of 2°C or 10°C/min becomes an IL belonging to the third group when it is quenched.
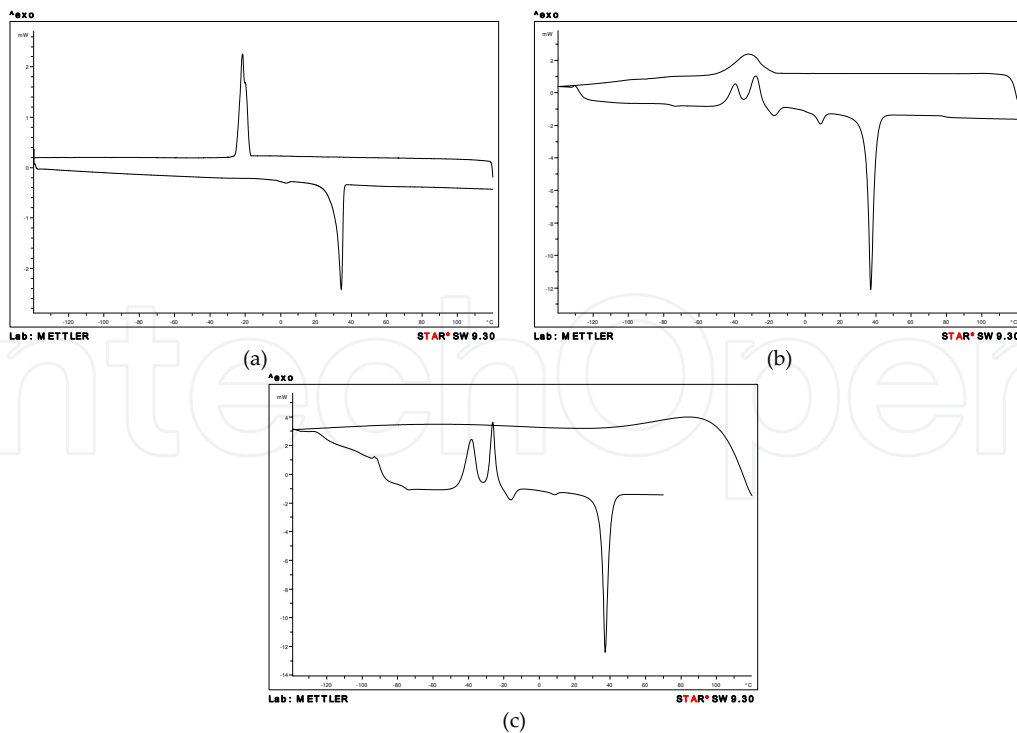

Figure 5. Thermogram of the ionic liquid BMpyTFO [12] cooling from 120°C to -140°C, followed by heating from -140°C to 120°C at (a) 2°C/min; (b) 10°C/min; (c) cooled by quenching at 40°C/min and heated at 10°C/min.

2.3. Influence of the rate on phase transitions

In Figure 6, a thermal scan of the ionic liquid PMpyNTf$_2$ at cooling and heating rates of 2°C/min and at 10°C/min is presented as an example of the effect of the cooling and heating rate on the glass transition. As can be seen, an increase in the rate leads to higher glass transition temperatures, both upon cooling and heating.
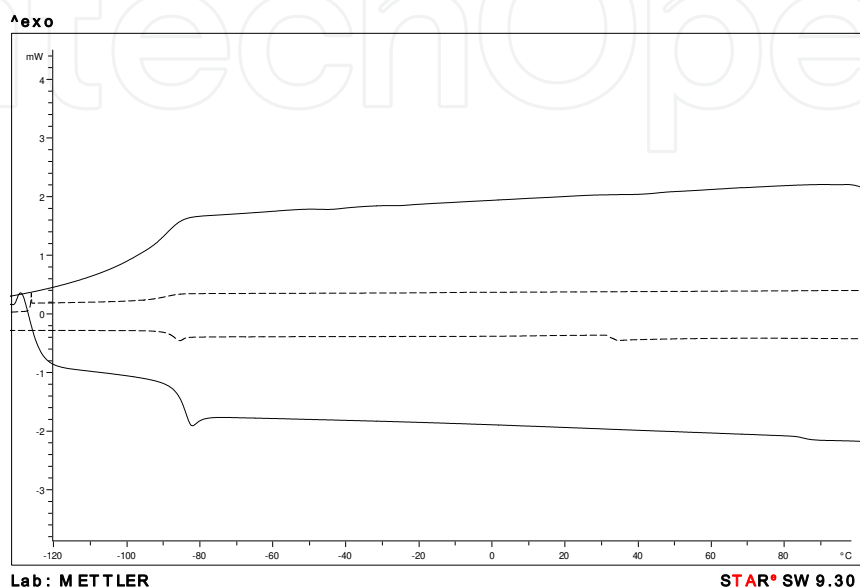

Figure 6. Thermogram of the ionic liquid PMpyNTf$_2$ [12] cooling from 120°C to -140°C, followed by heating from -140°C to 120°C at 2°C/min (dashed line) and at 10°C/min (solid line).
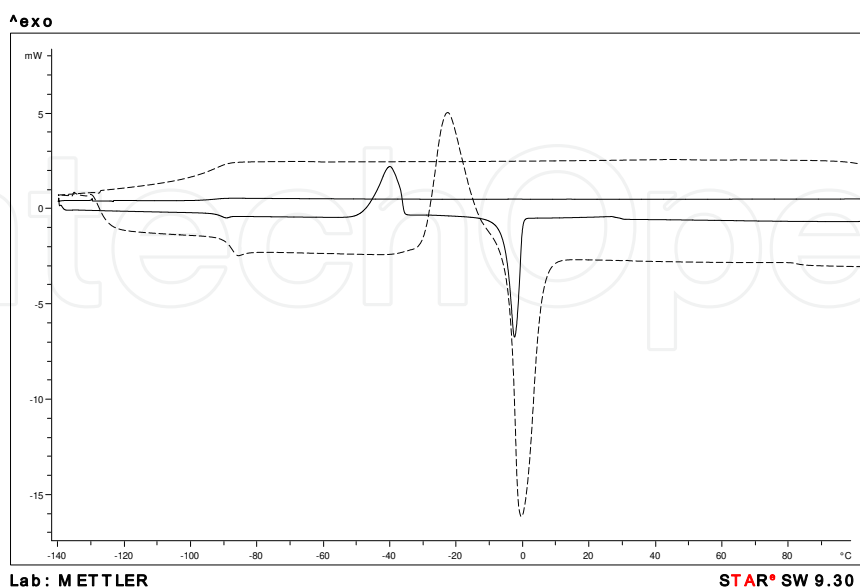

Figure 7. Thermogram of the ionic liquid BMimDCA [12] cooling from 120°C to -140°C, followed by heating from -140°C to 120°C at 2°C/min (solid line) and at 10°C/min (dashed line).

Figure 7 shows the influence of the heating rate on Tg, Tcc and Tm. In this example, it can be observed that an increase in the heating rate caused the cold crystallization transition to shift to a higher temperature. Here it can also be seen that, as previously explained in the work methodology section, by increasing the scan rate the cold crystallization and melting peaks overlapped.

As expected, the scan rate did not affect the melting temperature since, as is well-known, the melting temperature of a certain crystal does not change along with the heating rate.

Regarding the influence of cooling rate on the freezing transition, it must be taken into account that nucleation and crystal growth are somehow probabilistic events; thus, the determination of the freezing temperature is not always reproducible. This means that for an IL that suffers freezing upon cooling, when performing the same method for the same IL sample, the freezing peak might not occur at the same temperature.

3. Heat capacities

Heat capacity (c_p) is defined as the amount of energy required to raise the temperature of 1 g (or 1 mole) of a substance by 1 K. From this definition, it can be inferred that heat capacity is an important property for estimating the heating and cooling requirements of a substance and is therefore vital for the application of ILs in industrial applications.

In order to analyse the heat capacity values published in the literature for pure ionic liquids, several factors need to be taken into account. On determining heat capacities, different apparatuses can be used, such as adiabatic calorimeters (AC), differential scanning calorimeters (DSC), modulated DSC (MDSC) or Tian-Calvet DSC (TC). For the determination of the heat capacities of ionic liquids, a desirable characteristic in the technique used is for a small amount of IL to be enough for the determination of its heat capacity. In this context, the DSC and MDSC use much smaller samples than the adiabatic calorimeter or Tian-Calvet DSC. Between these two calorimeters, the MDSC has the advantage that it permits the separation of the signals into their thermodynamic and kinetic components, separating overlapped effects.

In the past few years, due to the simplicity of the technique and the small amount of sample required, DSC has been widely used in the determination of heat capacities. With this technique, different methods can also be followed, i.e., those directly calculating c_p values, the direct and the steady state methods, methods using a reference for calculating the sample c_p, as well as the ADSC and the sapphire methods. The sapphire method is more frequently used due to its higher accuracy [11].

Besides the experimental technique and method used, other variables should be considered for analysing heat capacity values. Among these variables that can affect the experimental values are sample size, the mass of the different crucibles used for the sample and as reference, the interval in which the measurement is carried out and the heating rate; these factors should be considered in addition to the usual considerations concerning the purity and dryness of the ionic liquid sample.

In this section, a proper methodology for the determination of heat capacities of ionic liquids using DSC with the sapphire method is suggested and the influence of the structure of the ionic liquid on this property is discussed.

3.1. Research methodology

As different techniques and methods have been used in the literature for the experimental determination of heat capacities and especially because in many of these studies not all the variables have been stated, the comparison among the values from different studies is particularly difficult. Consequently, taking into account the different aspects that need to be considered, a research methodology for the determination of heat capacities of pure ILs using differential scanning calorimetry and the sapphire method is proposed. A brief description of the sapphire method is provided here to gain a better understanding of the research method-ology: in the sapphire method, the DSC signal of the sample was compared with the DSC signal of the calibration sample (sapphire), which had a known specific heat. A total of three measurements were needed for this method: blank measurement (empty crucible), sapphire measurement and the sample measurement.

i.   Sample preparation.

   a.   **Weighing**. The accuracy of the weighing is very important in any measurement of heat capacity; it is vital to carry out all weighing in a precise balance. In the case of the sapphire method, an error in the weighing step will affect the weight of the sample, sapphire and reference crucibles, dramatically increasing uncertainty in the measurement of the heat capacities.

   b.   **Sample size**. It is believed that for the determination of heat capacities, the bigger the sample amount the better, since the signal size is proportional to the sample amount; nevertheless, it should be taken into account that the sapphire method uses a reference compound for the determination of c_p. This means that more reliable results will be obtained when the sample signal is closer to the reference signal (sapphire signal). The differences in the chosen sample size by different authors may be an explanation for the different values obtained for heat capacity for the same ionic liquid. In summary, the quantity of sapphire and sample size should be chosen for yielding signals as close as possible (within the limits recommended for the determination of c_p in the DSC, usually 40-80 mg); therefore, it was desirable that all weighing results involved in the experimental determination of this property were given in the studies.

   c.   **Crucibles**. The crucibles used for the sample, sapphire and as reference must be in perfect condition, without deformations, especially at the bottom. The use of a pinhole in the lid avoids pressurization inside the crucible and allows the evaporation of water and/or impurities in the dry step.

   To minimize errors, it is advisable that the weight of the three crucibles used for each measurement (sample, sapphire and reference) be as similar as possible.

    d. **Sample placement**. Good contact between the sample and the crucible bottom must be assured.

ii. Method. For the determination of heat capacities using the sapphire method, an initial isothermal stage (usually 10-15 minutes), followed by the heating stage to a final temperature, at which point there is another isothermal stage (usually 10-15 minutes), is common practice.

    a. **Dry step**. Similar to the thermal analysis method, a previous dry step is advised prior to the determination of the heat capacities of a pure ionic liquid.

    b. **Temperature range**. With regards to taking the c_p values, it must be taken into account that after the initial isothermal segment, some time is needed for the sample to reach a state of dynamic equilibrium; hence, the results obtained at the beginning of the dynamic segment should be discarded. It is also advised that the temperature range does not exceed 90°C. The heat capacity should not be determined during first order transitions in the physical state, for example during a crystallization transition. With the sapphire method, it is recommended that the heat capacities of the liquid and solid states be determined in separate runs, i.e., melting temperature should not be included in the chosen temperature range of the method.

    c. **Heating rate**. A heating rate of 10°C/min was usually used in the classical c_p measurements; however, nowadays, a heating rate of 20°C/min is generally used as this yields good results and saves time.

    d. **Repetition of measurements**. It is advisable practice to repeat the heat capacity measurements and to take the mean value as the final result.

    e. **Sapphire sample**. Although the crucible with the sapphire disks can be used in several runs, its c_p values must be checked regularly.

In general, the more common method for the determination of c_p in the literature consists of an isothermal segment at 0°C for 15 minutes, followed by a dynamic segment from 0°C to 90°C at 20°C/min and a final isothermal segment at 90°C for 15 minutes (considering that the IL is liquid in this range). Since the most required c_p value is a value corresponding to 25°C and taking into account that the first part of the dynamic segment is needed to reach a state of dynamic equilibrium, a method in which the temperature ranges from -15°C to 75°C (again considering that the IL is liquid in this stage) will assure obtaining a reliable value at 25°C.

3.2. Influence of the structure of the IL on heat capacity

Taking all the variables in the determination of heat capacities into account and analysing the c_p literature data for different structures, the influence of the cation, anion and alkyl-side chain of the cation on this property can be analysed. Due to the different techniques and methods used in literature and as mentioned above, the fact that many variables are not usually specified in the corresponding papers, to gain an overview of the influence of the ionic liquid structure

on this property it is more reliable to compare values obtained by the same authors instead of using different sources.

Heat capacity provides information about the amount of energy per molecule that the compound can store before the temperature of the compound increases; this energy is stored in translational, vibrational and rotational modes. As such, it is logical to assume that a molecule containing more atoms will have more energy storage modes and thus, higher heat capacity. Taking this into consideration, the following is an analysis of the influence of the different variables such as the different structures of the ionic liquids and the temperature on the heat capacity values.
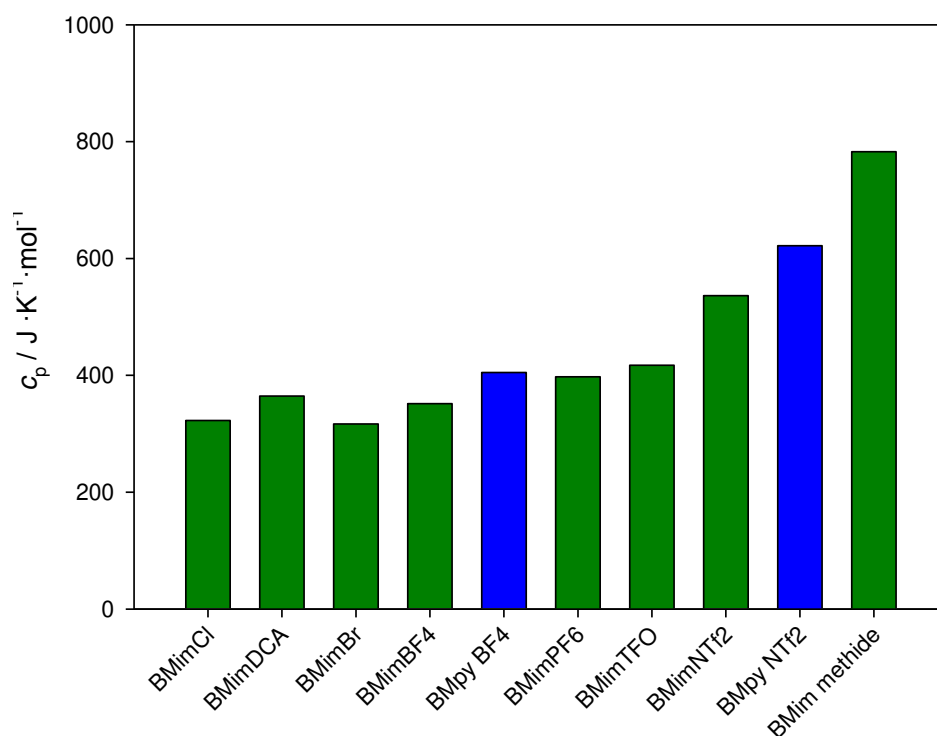

Figure 8. Heat capacities of several ionic liquids.

Considering the influence of the anion in the ionic liquid on heat capacity values, from the literature, it could be inferred that the c_p values were clearly affected by the anion, the general trend being that the higher the molar mass or number of atoms of the anion, the higher the heat capacity [6,10,11,13]. In general, the anions more frequently studied are bromide, chloride, tetrafluoroborate, hexafluorophosphate, trifluoromethanesulfonate, dicyanamide and bis(trifluoromethylsulfonyl)imide, usually attached to imidazolium-based ionic liquids, of which there is the most extensive data in the literature. The limited studies of pyridinium and pyrrolidinium-based ionic liquids usually agree with the results obtained for the wider studies on imidazolium ILs. In summary, for ILs containing similar cations and alkyl-side chains of the cation, the values for heat capacities increase with the molar mass of the anions [6,10], despite the fact that there are studies indicating that this general trend is not always followed [14].

The influence of the structure of the cation has been less studied than the influence of the anion; however, it can nonetheless be concluded that the pyridinium and pyrrolidinium-based ionic liquids present higher heat capacities than analogous imidazolium-based ILs [12, 15]. However, unlike the influence of the anion and alkyl-side chain length of the cation, which many studies have observed, in this case, the need for new experimental data in order to draw better conclusions was clear. In Figure 8, the influence of the anions on the c_p values of the 1-butyl-3-methylimidazolium and 1-butyl-3-methylpyridinium-based ionic liquids is presented, showing that in general, the c_p values increased when the molar mass of the anion increased. Comparisons of the ionic liquids with different cations (BMpyNTf$_2$/BMimNTf$_2$ and BMpyBF$_4$/BMimBF$_4$) can also be observed.

In the case of the influence of the alkyl-side chain length of the cation, the experimental results from published works indicate that the addition of a −CH$_2$− group leads to an incremental increase in the c_p of approximately 30-35 J/K mol [11,13,16], a similar value to that found for liquid alkanes, indicating that the alkyl-side chains of the ILs are similar in structure to those in liquid alkanes [16]. Moreover, it can also be concluded that the addition of a −CH$_2$− group has more influence at higher temperatures [11,16]. The influence of the alkyl-side chain length of the cation in the ionic liquid for 1-alkyl-3-methylimidazolium-based ionic liquids with alkyl = ethyl, butyl, hexyl and octyl on the c_p values is plotted in Figure 9, where it can be observed that an increase in the alkyl-side chain length means an increase in c_p values.
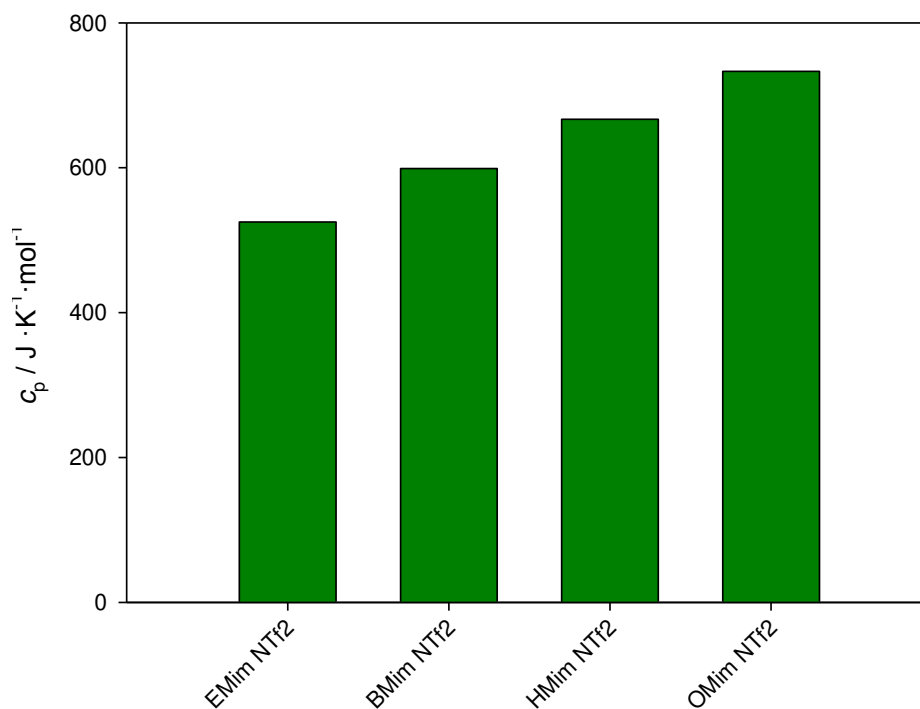

Figure 9. Heat capacities of 1-alkyl-3-methyilimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids.

Finally, regarding the fitting of heat capacity values as a function of temperature, these values are generally adjusted to a polynomial expression, usually of a second, third or even fourth

degree, depending on the temperature range taken for their determination. For example, if the temperature range of the method ranges from 0°C to 90°C and the c_p values are taken from 0°C to 90°C, it is probable that a third or fourth degree polynomial expression can be used for the fitting; however, if the c_p values are taken from 20°C to 80°C (neglecting the first minutes to avoid stabilization errors), a first or second degree polynomial expression will provide a proper fitting.

4. Thermal properties estimation

Due to the broad number of ILs, the experimental determination of the thermal properties of all these compounds is not possible; consequently, in order to enhance the selection of task-specific ionic liquids, several methods for estimating the melting temperature, the glass transition temperature or the liquid heat capacity of ILs have been developed, most of them based on the use of quantitative structure-property relationships (QSPR) or on group contribution (GC) methods. The following is a brief description of these methods and their application to Tm, Tg and c_p.

4.1. QSPR and GC methods

4.1.1. QSPR methods

QSPR methods are based on the relationship between the molecular characteristics of a compound and its macroscopic properties. Molecular descriptors, used for characterizing the microscopic properties of compounds, along with experimental data of the property (Tm, Tg, c_p, etc.) for a large number of compounds are needed in order to obtain an expression that will allow for predicting the value of this property for different compounds. A large number of descriptors exist for characterizing molecules; thus, the selection of the more significant among them is one of the main drawbacks of the model. These molecular descriptors, usually calculated using software packages such as DRAGON and CODESSA, can be classified using quantum chemical, electronic and geometrical descriptors that provide information about polar- or hydrogen-bonding interactions, as well as constitutional descriptors that characterize the chemical composition of the molecule and that does not depend on geometric and topological descriptors (TIs) that take into consideration the connectivity of atoms within a molecule [17]. In order to find essential information about molecule structure, a geometric optimization is generally the first stage. The general equation for QSPR methods [17] can be written as:

$$y_0 = b_0 + b_1 x_1 + b_2 x_2 + \ldots + b_p x_p \tag{1}$$

where y is the dependent variable (e.g., Tm, Tg or c_p), x_1, x_2…x_p are the independent variables (the descriptors), b_1, b_2,…,b_p are the regression coefficients and b_0 is the intercept.

The quality of the experimental values selected for developing a model is essential for obtaining good results. The main criteria for selecting the experimental values for the data set are the number and the diversity of available data, and these should have been measured under the same conditions, with enough reproducibility and accuracy [17]. The selected data are divided in the training set to develop and train the correlation equation and the test set for determining the predictive ability of the model for compounds that have not been used to develop it.

In order to obtain the relationship between molecular descriptors and the macroscopic property, several models such as neural networks (NN), decision trees, partial least squares (PLS) and multiple linear regressions (MLR) are usually employed. The squared correlation coefficients, R^2, squared cross-validated correlation coefficients R^2_{CV} and the Fisher criterion value, F, are generally used to assess the quality of the model. Special care must be taken for data points that have been poorly predicted, because this can indicate that the data were incorrectly measured or that the model has failed to include some important characteristics of the compounds [18].

4.1.2. Group contribution methods

Other methods widely used for the estimation of thermal properties are GC methods, which assume that a molecule is formed by several functional groups and the properties of a compound can be estimated as the sum of the contributions of all the functional groups that form the molecule. The contribution of each group to a property (e.g., Tm, Tg or c_p) is obtained from the experimental data of this property and determined for other substances that contain the same functional group. The main problem of this approach is that the way in which it defines groups is not unique; this is the reason why different authors have defined different groups to represent the same compound. Regarding ILs, some GC methods take the imidazolium or pyridinium rings as a group, whereas others divide the ring into many CH and N groups. According to Wu and Sandler [19] the geometry of the functional group should be the same, regardless of the molecule in which the group appears; it should have the same charge in all molecules and it should be the smallest identity into which the molecule can be divided in electroneutral groups. The general form of these methods [20] can be written as:

$$y = \left(\sum_i m_i D_i \right)^a + \left(\sum_j n_j E_j \right)^b + \left(\sum_k p_k F_k \right)^c \tag{2}$$

where y is the dependent variable (e.g., Tm, Tg or c_p), D, E and F are the contribution of the functional groups of order 1,2 and 3, respectively and m, n and p are the times that groups i, j and k appear in the compound. When $a = b = c = 1$ the model is lineal; when any of these numbers are zero, the corresponding contribution is not taken into consideration and if they are other values, the contributions are nonlinear. In the first-order GC methods, the groups behaved as if they were isolated and the effect of neighbour groups was not considered. In the second order GC methods, some information about the molecular structure was included with the purpose of including proximity effects and differentiating among isomers. The third level was

more convenient for the estimation of properties in the case of complex heterocyclic or large poly-functional acyclic compounds [20].

A summary of some of the QSPR and GC models were developed for the estimation of melting points, glass transition temperature and the heat capacity of ILs, and is presented below.

4.2. Melting point estimation

ILs are characterized by their low melting temperatures that depend on the strength of the crystal lattice, which is controlled by several factors such as charge distribution on the anions, H-bonding ability, the symmetry of the ions and the van der Waals interactions. Since it is an important property in the potential applications of ILs, several methods of melting temperature estimation can be found in the literature, most of them based on QSPR methods.

4.2.1. QSPR methods

The first attempt to predict the melting temperature of ILs was made by Katritzky et al. [21]. From a database of 126 pyridinium bromides and optimizing only the cationic part, they developed a six-descriptor equation, obtaining a value of $R^2 = 0.788$. According to the authors, the most significant descriptors were, the indices reflecting the coordination ability of the cation, the average nucleophilic reactivity index for the N atom related to electrostatic intermolecular interactions and the total entropy per atom related to the difference in conformational and rotational degrees of freedom in solid and liquid phases. Many other models [22-29] have been developed for several families of ILs (Table 2), most of them for imidazolium-based ILs with the same anion; consequently, their range of application is quite limited.

A different approach in the selection of the ILs was made by López-Martin et al. [30]. In this case, 22 ILs with the same cation, the 1-ethyl-3-methylimidazolium and 22 different anions were chosen, and the cation and anion geometries were optimized. The main disadvantages of this approach are that the cation-anion interactions are not taken into consideration and that the geometry optimizations correspond to the gas phase. The nine selected descriptors quantify the influence of size, branching, charge distribution and symmetry of the anion, as was previously reported for the cation. In order to test the effectiveness of this approach ($R^2 = 0.955$), a new data set including 62 ILs with 22 different cations and 11 different anions was correlated and a six-descriptor equation ($R^2 = 0.869$) was proposed.

Varnek et al. [31] performed an exhaustive study of QSRP models for melting temperature calculation. A data set with 717 bromides of nitrogen containing organic cations (126 pyridinium bromides, 384 imidazolium and benzimidazolium bromides, as well as 207 quaternary ammonium bromides) with melting temperatures from 5°C to 320°C was selected and results obtained using different machine-learning methods (associative neural networks, support vector machines, k nearest neighbours, modified version of the partial least-squares analysis, backpropagation neural network and multiple linear regression), while different types of descriptors were analysed. The study concluded that the most efficient descriptors/methods combination depends on the data set used. Slightly better results were obtained with neural networks and support vector machine methods, regardless of the chosen parameters. Regard-

ing the descriptors, the study concluded that the performance of the descriptors depends both on the machine learning method and the data set.

Structures	No. of ILs	No. of parameters	R^2	Ref.
Pyridinium bromides	126	6	0.7883	21
Imidazolium bromides	57	5	0.7445	22
Imidazolium bromides	29	5	0.7517	22
Imidazolium bromides	18	3	0.9432	22
Benzimidazolium bromides	45	5	0.6899	22
N-pyridinium bromides	126	5	0.790	23
Tetraalkyl-ammonium bromides	75	6	0.775	23
(n-Hydroxyalkyl)-trialkyl-ammonium bromides	34	5	0.716	23
1-susbstituted 4-amino-1,2,4-triazolium nitrocyanamides	7	1	0.960	24
1-susbstituted 4-amino-1,2,4-triazolium bromides	13	3	0.914	25
1-susbstituted 4-amino-1,2,4-triazolium nitrates	13	3	0.933	25
Imidazolium hexafluoroborates	29	6	0.9207	26
Imidazolium tetrafluoroborates	19	3	0.9047	26
Imidazolium bromides	30	4	0.89	27
Imidazolium chlorides	20	3	0.88	27
Imidazolium bromides and imidazolium chlorides	50	4	0.88	27
Pyridinium bromides, imidazolium bromides, benzimidazolium bromides and 1-susbstituted 4-amino-1,2,4-triazolium nitrates	288	8	0.810	28
Guanidinium chlorides, guanidinium bromides, guanidinium iodides and guanidinium tetraphenylborate	101	92	0.815	29

Table 2. Some QSPR models for the estimation of melting temperature.

For the purpose of ensuring a reliable prediction for a broad range of ionic liquids, the melting temperature of 705 ILs including sulfonium, ammonium, pyridinium, 1,3-dialkyl imidazolium, tri-alkyl imidazolium, phosphonium, pyrrolidinium, double imidazolium, 1-alkyl imidazolium, piperidinium, pyrroline, oxazolidinium, amino acids, guanidinium, morpholinium, isoquinolinium and tetra-alkyl imidazolium was collected by Farahani et al. [32]. The final proposed equation (R^2 = 0.658) contained 12 descriptors, eight of them describing the characteristics of the cation and the other four the characteristics of the anion.

Yan et al. [33] proposed an equation using topological indices based on atom characters (atom radius, atom electronegativity, etc.) and atom positions in the hydrogen suppressed molecule

structure. The data set was composed of 394 ILs: 120 imidazolium, 43 benzimidazolium, 109 pyridinium, 19 pyrrolidinium, 65 ammonium, seven sulfonium, 20 triazolium and 11 guanidinium. The resulting equation incorporates 12, 14 and six TIs for the cation, the anion and their interaction, respectively, the obtained value being $R^2 = 0.778$ for the training set and 0.753 for the test set.

4.2.2. Group contribution methods

A group contribution method for the calculation of melting temperatures of ILs was developed by Huo et al. [34] for 155 imidazolium and benzimidazolium ILs. The structural groups, up to a total of 30, were selected in a way that rendered them as small as possible and considering three group types: belonging to a ring, belonging to a no-ring structure and ionic groups. In addition to the structural groups, three characteristic factors were included: (1) σ, which took the values 0 or 1, depending on whether the groups connected to a N atom in an imidazolium ring were the same or different; (2) τ, which was the number of ring groups in the molecule; (3) δ, which could be 0 if there was no group attached to the C2 position in the imidazolium group or 1 if one group was attached. The average relative deviation in this work was 5.86% and deviations of less than 5% were obtained for 106 ILs. The maximum relative deviation was 32.75% for 1,3-dimethylimidazolium chloride.

Using a first-order contribution approach and considering the whole ring as a single group, another group contribution method was proposed by Lazzús [35] using a set of 400 ILs. The group contribution to the melting point was calculated for 31 groups for the cation and 32 groups for the anion, and covered a broad range of ILs. The average relative absolute deviation reported was less than 8% for the 200 ILs used for the group parameters calculation and less than 6% for the other 200 ILs used in the prediction stage.

The most comprehensive melting temperature database was collected by Gharagheizi et al. [36] in order to amplify a GC model with a broad range of applicability. The melting temperature of 799 ILs including 1,3-dialkylimidazolium, 1-alkyl imidazolium, amino acids, ammonium, double imidazolium, guanidinium, isoquinolinium, morpholinium, oxazolidinium, phosphonium, piperazinium, piperidinium, pyridazinium, pyridinium, pyrrolidinium, pyrroline, quinary alkyl imidazolium, sulfonium, tetra-alkyl imidazolium, tetrazolium, thiazolium, tri-alkyl imidazolium, triazolium and uronium was collected and the group contribution for 80 groups (31 anions and 49 cations) were calculated. Some of these groups were not structural groups, because they were defined as the "sum of all the carbons belonging to any aromatic and heteroaromatic structure" (group 6) or the "total number of Ns, Os and Fs in the molecule, excluding N with a formal positive charge, higher oxidation states and pyrrolyl forms of N" (group 13), among others [36, p. 3]. The absolute average relative deviation was 5.82%.

Recently, Valderrama [37] reviewed some of the models proposed for the estimation of melting point [34, 36, 38] and concluded that the experimental determination of melting temperature should be standardized in order to guarantee reproducibility, and further emphasized that even if the data were accurate, none of the present methods serve as a clear solution to the problem of predicting the melting temperatures of ILs.

4.3. Glass transition estimation

Glass transition can be defined as the transition of an amorphous material from a hard and relatively brittle state into a molten or rubber-like state. This transition is accompanied by changes in some properties such as heat capacity and thermal expansibility. Even though many ILs present only glass transition, few models have been developed for their estimation compared to melting temperature. The QSPR and GC methods available in the literature are summarized below.

4.3.1. QSPR methods

Some QSPR-based models for predicting the Tg of ILs have been reported in the literature. Many of them were developed for predicting the glass transition temperature of one family of ILs such as ammonium [39] or 1,3- dialkylimidazolium [40, 41]. In these cases, the Tg is calculated as the sum of the contribution of the anion and the cation, and their corresponding descriptors are included in $T_{g,a}$ and $T_{g,c}$ terms:

$$T_g = \text{intercept} + T_{g,a} + T_{g,c} \tag{3}$$

The model developed for ammonium-based ILs [39] contains 12 descriptors (six for the cation and six for the anion) obtained from the experimental data of 73 ILs (22 different anions and 49 different cations) and the reported R^2 value is 0.9657.

A database of 109 1,3- dialkylimidazolium ILs was selected by Mousavisafavi et al. [40, 41] to develop two models applying both a linear and a nonlinear approach for the selection of the molecular descriptors; similar results were obtained in both cases. The best value of R^2 was 0.91, achieved using the nonlinear approach.

A more general equation was developed by Mirkhani et al. [42] and included 139 ILs (37 different anions and 86 different cations including alkylimidazolium, amino acids guanidini-um, isoquinolinium, morpholinium, oxazolidinium, phosphonium, piperidinium, pyrrolidi-nium and triazolium) in the database. They proposed an equation with 11 descriptors (R^2 = 0.8897), three descriptors for the anion and eight descriptors for the cation. The highest and lowest prediction errors, 8.29% and 1.67%, belonged to 1-alkyl imidazolium and oxazolidini-um, respectively.

Similar to the estimation of Tm, Yan et al. [43] implemented a QSPR model based on topological indices (TIs) for Tg calculation. A total of 139 ILs including 63 imidazolium, 17 pyridinium, 48 ammonium, seven sulfonium and four triazolium were taken from the literature to develop the model. The resulting expression contained seven TIs for the cation, 16 TIs for the anion and two TIs for their interaction; the overall value for R^2 (0.898) was very close to the value obtained using other descriptors [42].

4.3.2. Group contribution methods

To date, three GC models have been proposed for Tg estimation. One of them is only suitable for 1,3-dialkylimidazolium ionic liquids [44], while the other two [45,46] are appropriated for many types of ILs. In all cases, the IL ring (imidazolium, pyridinium pyrrolidinium, etc.) is considered as a group. The general equation can be written as:

$$T_g = T_{g0} + \sum_{i=1}^{N_a} N_{ai} T_{gai} + \sum_{i=1}^{N_c} N_{ci} T_{gci} \tag{4}$$

where N_{ai} and N_{ci} are the occurrence of the i group in the cation and in the anion, T_{gai} and T_{gci} are the contributions of the group i and T_{go} is the intercept.

From a data set of 496 ionic liquids (71 anions and 247 cations), Gharagheizi et al. [45] calculated the group contribution parameters for 19 anions and 31 cations. Similar to the method proposed for estimating Tm [36], some of the considered groups were not structural groups. The average absolute relative deviation obtained for the complete data set was 3.65%. Concurrently, Lazzús [46] published another GC model using 150 ILs and proposed the group interaction parameters for 26 cation and 36 anion groups. The average absolute relative deviation reported for the total set was 4.91%. None of these papers provide any indication of the criteria applied to the selection of the groups.

4.4. Heat capacity estimation

Knowledge concerning the heat capacity of ILs is important because of its relationship with other thermodynamic properties i.e., entropy, enthalpy and Gibbs free energy, and also due to the application of ILs in industrial processes or as heat transfer fluids. A brief summary of the c_p estimation methods is presented below.

The relationship between c_p and molar volume has been stated by several authors and some expressions for the calculation of c_p at 25°C have been developed [47, 48]. Including the temperature as a variable, Paulechka et al. [49] proposed another equation that allows to calculate the c_p values at other temperatures.

The only method based on QSPR found in the literature was proposed by Sattari et al. [50]. A database containing the c_p values of 82 ILs including 39 different cations and 24 anions was used to find the most accurate model with an acceptable number of descriptors. In the final 13-parameter equation, a binary combination of two descriptors instead of a single descriptor was included in equation 1. On the basis of the R^2 values for the training set and the test set (0.990, 0.996), the authors suggest that binary multiplication of the descriptors can be a successful approach.

The first GC method for the estimation of c_p of ILs was developed by Gardas and Coutinho [48] using a second-order group additivity approach. The database was composed of 19 ILs that permitted the calculation of the group contribution parameters for four cations and six anions. According to the authors, these group parameters made it possible to calculate the c_p of at least

200 ILs and in almost all cases, the deviations in predicted heat capacities were inferior to the experimental uncertainties. The group contribution parameters were subsequently extended to amino acid-based ILs by Gardas et al. [51].

Ge et al. [13] adapted the Joback [52, 53] GC method for the prediction of the ideal gas heat capacities of molecular compounds to the estimation of c_p of ILs. From the ideal gas heat capacities and using an estimation method [54] to calculate the critical properties and the acentric factor, the c_p can be calculated. The original parameters [52], along with the parameters calculated for three new groups (B, P, -SO-), were used to predict the c_p of 53 ILs, leading to a relative absolute deviation of 2.9%.

A different approach to the estimation of c_p using a GC method was proposed by Valderrama et al. [55] and combines the group contribution method with mass connectivity indices, which considers the type of connection between groups and the mass of these groups. In order to build a more general method, the database employed for determining the value of the contribution of the groups included 32 ILs of five families (imidazolium, pyridinium, pyrrolidinium, phosphonium and alkyl-ammonium) and 126 organic compounds. The average absolute deviation values were 2.8% in the correlation of the 32 ILs and the 126 organic compounds, and 2.1% in the c_p prediction of nine ILs.

The temperature dependency of c_p for several ions was calculated using a quadratic equation by Müller and Albert [56]:

$$Cp_{ion} = A + BT + CT^2 \tag{5}$$

$$Cp_{IL} = \sum_{i=cations} x_i Cp_i + \sum_{j=anions} x_j Cp_j \tag{6}$$

where A, B and C are the parameters of the anion or cation and x_i and x_j are the molar contributions of the cation or anion on all cations or anions, respectively. The parameters were calculated for 39 cations and 32 anions from a database of 84 ILs. The average absolute deviation was 1.4% and 4.4% for the training set and the test set, respectively.

In addition to the model previously mentioned [50], Sattari et al. [57] presented another model for calculating c_p using a set of parameters such as the number of atoms, of non-h-atoms and of five-membered rings. Four of these 14 parameters were the same as those selected in the QSPR-based model. The average absolute deviation for the 82 ILs included in the database was 1.68%.

For the purpose of deriving an easy-to-use correlation based on very simple molecular parameters, Farahani et al. [58] proposed a correlation equation that only depends on the atom counts in both anion and cation, the number of hydrogen in anions and the number of methyl groups in the cation. In this case, the absolute average relative deviation reported by the authors was 2.48%.

5. Conclusions

Although the use of DSC for the thermal analysis and the experimental determination of the heat capacities of pure ionic liquids is a widely-used technique, there are several factors that have an influence on their correct determination. For this reason, in this chapter, not only was a work methodology proposed for the determination of both phase transition temperatures and heat capacities, but the possible aspects affecting their experimental determination have also been explained.

Attempting to standardize the work methodology is necessary for obtaining high quality and precision-based experimental data, as well as for carrying out comparisons between the results presented by different authors, which will allow for reliable conclusions.

Due to the different results observed in the thermal analysis of the pure ILs characterized thus far, finding a relationship between the structure of the IL and its thermal behaviour is complicated. For this reason, in this chapter, the thermal behaviour of pure ILs was divided into three types, depending on the phase transitions presented by each IL:

i.   The first type of behaviour is formed by ionic liquids characterized by presenting only the formation of amorphous glass.

ii.   The second type of behaviour is characterized by presenting a freezing transition, forming crystals upon cooling and a melting transition upon heating.

iii.   The third type of behaviour in the ILs that does not show a tendency to crystallize upon cooling; however, upon heating, they exhibit cold crystallization.

It is important to state that ionic liquids usually present polymorphic-like behaviour, increasing the difficulty of interpreting the DSC thermograms. Additionally, the phase transitions are strongly dependent on the scanning rate and on the cooling method used to obtain the solid phase (quenching or slow cooling).

The relatively extensive database on the heat capacities of pure ILs allows for drawing some conclusions about the influence of the structure of the ionic liquid on heat capacity values. The c_p values are clearly affected by the nature of the anion, the general trend being that the higher the molar mass or number of atoms of the anion, the higher the heat capacity. In the case of the influence of the structure of the cation, although it has been less studied than the influence of the anion, it can be concluded that pyridinium and pyrrolidinium-based ionic liquids present higher heat capacities than their analogous imidazolium-based ILs. As for the influence of the alkyl-side chain length of the cation, the addition of a $-CH_2-$ group leads to an incremental increase in the c_p of approximately 30-35 J/K mol and this influence is more remarkable at higher temperatures.

Finally, regarding the estimation of the melting and glass transition temperatures, and liquid heat capacities, although several methods for estimating the thermal properties of ILs can be found in the literature, most of them are based on the use of quantitative structure-property relationship (QSPR) or on group contribution (GC) methods; all of them present several

limitations, which can be attributed to two aspects: all experimental data have not been correctly determined and/or our knowledge of the factors that influence thermal properties is incomplete. A bigger effort should be made from both experimental and academic perspectives to improve the estimation of these properties.

Nomenclature of ionic liquids

$EMimNTf_2$	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$EMMimNTf_2$	1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide
$PMimNTf_2$	1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$BMimNTf_2$	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$BMimBF_4$	1-butyl-3-methylimidazolium tetrafluoroborate
BMimTFO	1-butyl-3-methylimidazolium triflate
BMimDCA	1-butyl-3-methylimidazolium dicyanamide
$BMimPF_6$	1-butyl-3-methylimidazolium hexafluorophosphate
BMimCl	1-butyl-3-methylimidazolium chloride
BMimBr	1-butyl-3-methylimidazolium bromide
BMim methide	1-butyl-3-methylimidazolium methide
$BMMimBF_4$	1-butyl-2,3-dimethylimidazolium tetrafluoroborate
$BMMimPF_6$	1-butyl-2,3-dimethylimidazolium hexafluorophosphate
$C_3CNMimDCA$	1-butyronitrile-3-methylimidazolium dicyanamide
$C_3CNMMimPF_6$	1-butyronitrile-2,3-dimethylimidazolium hexafluorophosphate
$HMimNTf_2$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
HMimDCA	1-hexyl-3-methylimidazolium dicyanamide
HMimTFO	1-hexyl-3-methylimidazolium triflate
$EMpyESO_4$	1-ethyl-3-methylpyridinium ethylsulfate
BpyBr	1-butylpyridinium bromide
$PMpyNTf_2$	1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide
$BMpyNTf_2$	1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide
BMpyBr	1-butyl-3-methylpyridinium bromide
BMpyTFO	1-butyl-3-methylpyridinium triflate
$BMpyBF_4$	1-butyl-3-methylpyridinium tetrafluoroborate
$HMpyNTf_2$	1-hexylpyridinium bis(trifluoromethylsulfonyl)imide
$BMpyrNTf_2$	1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
$C_3CNTMANTf_2$	butyronitrile-trimmethylammonium bis(trifluoromethylsulfonyl)imide

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