



Liquid–solid–liquid phase transition hysteresis loops in the ionic conductivity of ten imidazolium-based ionic liquids

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ABSTRACT

This paper extends previous ionic conductivity measurements to the phase transition between liquid to solid states, where we present measurements for increasing and decreasing temperatures. Data show the existence of hysteresis loops for some ILs, while others do not present any transition (at least it is not measurable). Seven of the studied ILs have 1-ethyl-3-methyl imidazolium (EMIM) as a common cation, which allows us to observe the anion influence, and four IL compounds have tetrafluoroborate (BF_4^-) as common anion and the 1-alkyl-3-methyl imidazolium as cation with four different alkyl chains (ethyl, decyl, dodecyl and hexadecyl). The hysteresis loop differs in shape and amplitude for the different IL compounds presented here, thus some of them present a closed hysteresis loop, without any jump in the value of ionic conductivity, while other ILs have a sharp decrease of the conductivity at a given temperature, and so they present open hysteresis loops. Those hysteresis loops are presented here for the first time and it is shown that they are different for the studied ILs. These measurements demonstrate the capacity of the ILs to maintain its liquid state characteristics (being so in a super cooled liquid state) when temperature decreases well below its melting point (up to 60 K for some compounds). We explain it as resilience of the pseudolattice structure already present in liquid state to become a rigid crystalline structure, typical of these ILs at solid state.

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1. Introduction

Ionic liquids (ILs) are defined as chemical compounds formed solely by ions and having melting points below 100 °C, but most usually around or below room temperature. The existence of an IL at moderate temperatures is not yet well understood theoretically, because the strong electrostatic forces among ions should provoke the collapse of the system to its solid state. The most probable cause of their liquid state comes from the large asymmetry in the sizes of cations and anions, which preserves a big attraction force between them. In contrast, if sizes are too big due to large alkyl chains, the Van der Waals forces become important and so melting temperature of the IL increases. The equilibrium between these two inter-molecular forces provoke that the lower melting temperature is achieved for the ILs with alkyl chains about five or six carbon atoms for any given IL family (in particular for the 1-alkyl-3-methyl imidazolium) [1].

As it is well known, many applications for ILs in the field of green chemistry have been proposed, and some of the most interesting

are related with electrochemical processes. Among them we can mention its use as charge transport medium in energy generators (e.g. Li batteries), as electrolytic media in electro-deposition processes [2,3], or even to improve solar cells, both as refrigerant fluid [4] and as an electrolyte for Dye-Sensitised Solar Cells (DSSC) [5]. In order to explore these numerous applications, it is first necessary to experimentally measure their most important physical magnitudes. Among them, the electrical (or ionic) conductivity is one of the characteristic magnitudes of ILs because they are the only pure liquids (excluding mercury) with electrical conductivity in the range of mS/cm at room temperature. In addition, this is a crucial magnitude to develop the proposed electrochemical applications of ILs [1–3,5]. Moreover, electrical conductivity data provide information about the density of free ions and their mobility, which is crucial to develop a theoretical model capable of explaining the data measured for each IL and to predict those not available. Some steps in this direction have been performed and, particularly, the Bahe–Varela theory, based in the existence of a pseudorectilinear arrangement of IL ions, is giving good results [6]. Since our first paper [7], where we demonstrate the Vogel–Tamman–Fulcher (VTF) behavior of the temperature dependence of electrical conductivity for ILs, a few more papers have published similar data [8–15] for more imidazolium based ILs, confirming in all cases our

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Nomenclature

List of symbols

A, B	fitting parameters
C	concentration
E_a	activation energy
k_B	Boltzmann constant
N	number of data points used to fit a given equation
n	number of carbon atoms of the alkyl chain
s	standard deviation
$s\%$	percentile standard deviation
T	temperature
T_0	Vogel temperature
T_f	freezing temperature
T_g	glass transition temperature
T_m	melting temperature
T_S	solidification temperature
κ	ionic (or electrical) conductivity
κ_∞	ionic conductivity at infinite temperature
κ_{cal}	calculated ionic conductivity
κ_{exp}	experimentally measured ionic conductivity

reported VTF behavior. Moreover, other paper focused on ionic conductivity of pyrrolidinium, pyridinium and ammonium based ILs [16] reported similar results. However, in all published papers appears data for decreasing temperatures in the liquid state but, at our knowledge, none of them covers the liquid–solid–liquid transition temperature region.

Here, we report experimental measurements of the electrical conductivity of ten imidazolium based ILs versus temperature at atmospheric pressure. The range of temperatures analyzed in this paper depends on each IL, and it was selected to include each melting transition and extending at least 100 K above and at least 50 K below it. The analyzed ILs were selected to have their melting points above room temperature because when melting temperatures are lower, the electrical conductivity value is very small in the transition, and near the conductivity resolution of 2 nS cm^{-1} . All the studied ILs are commercial, relatively cheap and among the most investigated for electrochemical applications [1–3]. The ILs measured can be classified in two different series: The first one allows us to study the anion influence, and it includes 1-ethyl-3-methyl imidazolium (EMIM⁺) with different anions such as chloride (Cl⁻) (two samples with different purity grade); bromide (Br⁻), iodide (I⁻), tetrafluoroborate (BF₄⁻) hexafluorophosphate (PF₆⁻) and tosylate (CH₃-C₆H₄-SO₃⁻, TS). The second group allows the study of the cation length influence, and they have common BF₄⁻ anion and different 1-alkyl-3-methyl imidazolium cation, with the alkyl chain being decyl (DMIM⁺), dodecyl (dDMIM⁺), and hexadecyl, (hDMIM⁺). Obviously, the EMIM–BF₄ belongs to both series. To the best of our knowledge, it is the first time that measurements like the ones presented here are reported, particularly the different hysteresis loop of the electrical conductivity in the liquid–solid–liquid phase transitions for each of the studied ILs. Additionally, data for the ionic conductivity in the solid phase of any IL have not been published before.

2. Experimental

Two of the chemicals used, EMIM–Br and one of the EMIM–Cl, are from Aldrich, and they present purities higher than 97% and 93% (BASF quality), respectively. The other seven ILs measured are from Solvent Innovations (actually absorbed by Merck), and all of them present a purity better than 98%. The main characteristics of the ILs used are included in Table 1, including purity, chemical

Table 1

Mean characteristics of the ionic liquids measured.

Ionic liquid	Purity	Molecular weight	Formula	Water content
EMIM–Cl	>99%	146.62	C ₆ H ₁₁ ClN ₂	297.8 ppm
EMIM–Cl	>93%	146.62	C ₆ H ₁₁ ClN ₂	<0.1%
EMIM–Br	>97%	191.07	C ₆ H ₁₁ BrN ₂	<0.1%
EMIM–I	>98%	238.07	C ₆ H ₁₁ IN ₂	<0.5%
EMIM–PF ₆	>99%	256.13	C ₆ H ₁₁ F ₆ N ₂ P	149.7 ppm
EMIM–TS	>99%	282.36	C ₁₃ H ₁₈ N ₂ O ₃ S	835.4 ppm
EMIM–BF ₄	>98%	197.97	C ₆ H ₁₁ BF ₄ N ₂	<0.1%
DMIM–BF ₄	>98%	310.18	C ₁₄ H ₂₇ BF ₄ N ₂	<0.1%
dDMIM–BF ₄	>98%	338.24	C ₁₆ H ₃₁ BF ₄ N ₂	<0.1%
hDMIM–BF ₄	>98%	394.34	C ₂₀ H ₃₉ BF ₄ N ₂	<0.5%

formulae, molar weight and water content. The ILs where used as they came from the dealers, and no further purification or analysis were performed. As it is well known, all the ILs used are hygroscopic, as recently measured quantitatively by some of us [17]. To avoid water contamination we have manipulated all compounds in an inert atmosphere chamber with dry air or Ar (being the relative humidity grade lower than 10%), where the measurement cell was inserted in a tube with the corresponding compound, and sealed before take it to the atmosphere to perform the measurement, since even a very small water quantity mixed with the IL is known to increase its electrical conductivity [18,19]. Water content certified by the dealer is included in Table 1 for all ILs used.

The ionic conductivity data (κ) reported here has been measured at a constant frequency of 500 Hz using a conductimeter from CRISON, model GLP31. We used two different measuring cells, one with a cell constant $C \approx 1 \text{ cm}^{-1}$ (indicated to measure ionic conductivity values from 5×10^{-3} to 100 mS cm^{-1}) and another one with $C \approx 0.1 \text{ cm}^{-1}$ (to measure values from 2×10^{-6} to 0.5 mS cm^{-1}). The resolution of the conductimeter with the indicated measuring cells (and within the corresponding range) is better than 1% of the measured value (with a minimum resolution of $2 \times 10^{-6} \text{ mS cm}^{-1}$). All data presented here have been measured several times in different samples to ensure its reproducibility, which is better than 5% in absolute value. Both measuring cells are formed by two parallel plane plaques covered with platinum oxide and they were used to measure both phases, liquid and solid. The detailed measurement procedure has been described previously [20]. Temperature of the sample was controlled using two different thermostatic baths. For measurements between -15°C and 120°C (258 K and 393 K) we use a Julabo F25 thermostat calibrated with an external sensor Crison T-637, while to measure samples below -15°C or above 120°C temperature control was achieved by means of a Lauda Pro-line RP 890 with a measurement range that extends from -95°C to 200°C (178–473 K). In both systems the temperature precision is better than 0.1 K. It is important to note that in this work all measurements were done by means of a static isothermal method, thus we wait about 15 min with the sample at constant temperature before any single measurement was performed. At the phase transition we waited for at least 30 min with the sample at constant temperature before measuring its κ , thus we let the sample perform the ionic rearrangement that happens at solidification. To illustrate this effect, we show in Fig. 1(a)–(c) the time evolution of the electrical conductivity of EMIM–Br when temperature of the thermal bath (in which the sample is immersed) is abruptly lowered by about 8 K (the exact temperature change appears in the corresponding figure). In Fig. 1(a) we observe the time evolution of κ when its temperature is reduced being the sample in its liquid state, in Fig. 1(b) when it is in solid state (note the difference in the κ value with previous figure), and in Fig. 1(c) temperature is reduced just at the transition between liquid and solid states (which we call here the solidification temperature, T_S). Far above or below T_S , the electrical conductivity of the IL reaches its final value after

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