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Quaternary phosphonium-based ionic liquids: Thermal stability and heat capacity of the liquid phase

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ABSTRACT

In spite of the great importance of calorimetric data on phosphonium-based ionic liquids (PBILs), the information available in the literature is quite limited. This work reports the study of the thermal stability and the determination of heat capacity of the following (PBILs): tributyl(methyl)phosphonium methyl sulfate, $[(C_4)_3PC_1][MeSO_4]$, trihexyl-tetradecylphosphonium chloride, $[(C_6)_3PC_{14}][Cl]$, trihexyl-tetradecyl-phosphonium dicyanamide, $[(C_6)_3\ PC_{14}][DCA]$, trihexyl-tetradecylphosphonium bis((trifluoromethyl)sulfonyl) imide, $[(C_6)_3\ PC_{14}][NTf_2]$, and trihexyl-tetradecylphosphonium tris(pentafluoroethyl) trifluorophosphate, $[(C_6)_3\ PC_{14}][FAP]$. Measurements on the well-known IL 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide, $[EMIM][NTf_2]$, were also performed for comparative purposes. The thermal stability was assessed by conventional and high resolution modulated thermogravimetric analysis within the interval (303 to 873) K. The heat capacity was measured by modulated differential scanning calorimetry within the range (310 to 515) K with an uncertainty in the range (1 to 5) $J \cdot K^{-1} \cdot mol^{-1}$. The experimental results were correlated using polynomial expressions. The Joback method for predicting ideal gas heat capacities was used in conjunction with the principle of corresponding states and the modified Lydersen–Joback–Reid method to predict the heat capacity of the ILs. The methods due to Valderrama *et al.* were also used with the same purpose.

1. Introduction

Ionic liquids (ILs) are three dimensional networks of ions which remain in their molten state at ambient temperature. They have the ability to dissolve a large variety of organic and inorganic substances, even polymers in high concentration, and tend to show a remarkable thermal stability. ILs are safe because usually they are non-toxic, have very low vapor pressure (below 1 Pa at 25 °C), and are non-flammable materials. These characteristics allow ILs to replace flammable and volatile organic solvents in chemical processes. Because of such sort of attributes ILs have been said nature friendly "green solvents" [1].

ILs are usually formed by a large cation and an inorganic anion. The number of possible combinations (cation/anion) is enormous, making the number of imaginable ILs virtually unlimited. This aspect makes ILs "designer solvents" with tunable physicochemical properties, such as density, viscosity, surface tension, thermal conductivity, and solubility of various liquid and gaseous solutes. Therefore, specific characteristics are possible for a large number of applications (e.g thermal and separation processes, electrochemical and catalytic applications). In quaternary phosphonium-based ILs (PBILs), the phosphorus atom permits the bonding with four different substituents. This give the chance of having cations with different structures (and physicochemical properties), which determine a rather large type of interactions. Also within the class of PBILs a great number of combinations cation/anion exists, allowing the tuning of thermophysical properties, but other practical advantages can be invoked, such as the low toxicity. Furthermore, PBILs are now available in large quantities and it is proved that are more stable and less expansive to manufacture [2–5] compared to most of imidazolium-based ILs.

While great attention has been dedicated to the physicochemical properties of imidazolium, ammonium and piridinium based ILs [6–9], very few investigations involving PBILs have been reported in the literature. This appears to be surprising taking into account the increasing applications in chemical reaction [10–12], namely in polymer synthesis [13], and as greener plasticizers for biomedical applications [14] in supercritical processes [15] in liquid phase extraction [16–18], gas solubility [19,20], electrochemical research [21,22], and tribology [23,24].

Heat capacity is one of the basic thermodynamic properties whose knowledge is critical for many engineering calculations, as is the case of the design of processes that include ILs as thermal storage media, such as solar thermal electric power systems [25], or in absorption heat pumps or chillers which are important units of air conditioning and refrigeration [26]. Because of the important role that thermophysical properties of ILs can play, some research

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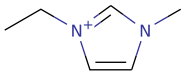
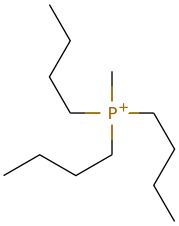
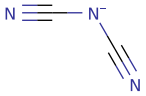


1-Ethyl-3-methylimidazolium

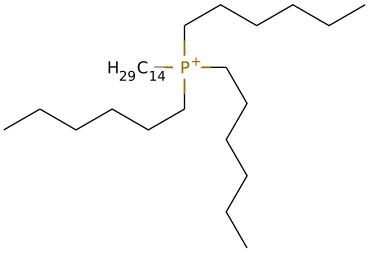
Chloride



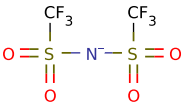
Tributyl(methyl)phosphonium



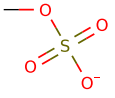
Dicyanamide



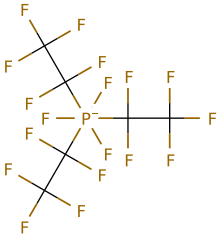
Trihexyl-tetradecylphosphonium



Bis((trifluoromethyl)sulfonyl)imide



Methyl sulfate



Tris(pentafluoroethyl)trifluorophosphate

FIGURE 1. Two dimensional structures of the cations and anions used in this study.

groups have started with systematic measurement and data collection on this kind of substances. At the present, the open access data compiled by the standard reference database of the national institute of standards and technology (NIST) in its ionic liquids database is the most exhaustive compilation of ILs heat capacities [27]. It contains raw heat capacity data, with assigned uncertainties, compiled from thermodynamic journals. The information provided by NIST, however, must be carefully used because the lack of a deep analysis and cross-checking underlying the compiled data. The choice of the most correct heat capacity data is difficult in many cases. As an example, we can take the data for [EMIM][BF_4] and [BMIM][BF_4]. The values of the heat capacity from different authors differ by more than 20% for the former imidazolium and by more than 10% for the latter. Recently Zábranký *et al.* [28] published a review where the experimental data of 50 ILs were evaluated and the recommended values presented. Very recently, Paulenchka [29] reported a survey of measured heat capacity of ILs in the liquid state. This critical review contains data for 102 ILs from 63 literature sources and covers the period from 1998 to February 2010. For the heat capacity of PBILs, to the best of our knowledge, only two references can be found referred to the determinations made by Gardas *et al.* [30] for amino acid based tetrabutylphosphonium ILs, and by Ge *et al.* [31] for [$(C_6)_3PC_{14}$][NTf_2]. Molecular dynamics simulations were made for this IL by Xiu *et al.* [6] and from this study the heat capacity was calculated among other thermophysical properties.

Experimental data for heat capacity of ILs are still scarce and limited to a few classes of ILs. More data and better understanding of heat capacity are needed to the "design" of ILs for specific applications and when experimentally measured data are not available the theoretical or empirical methods must be used to know if heat capacity is within acceptable limiting values defined by design specifications. The prediction methods are needed and are an attractive way of obtaining data to make faster progress on modeling, simulation and design of process involving ILs. Group contribution methods (GCMs) are commonly used to predict thermophysical properties in process design, and many have become an important part of process simulation software due to their wide applicability, ease of use, and sometimes good accuracy. To date, some prediction models of heat capacity by GCMs have been