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Data selection and estimation of the normal melting temperature of ionic liquids using a method based on homologous cations

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ABSTRACT

A simple method based on homologous series for data selection and estimation of the normal melting temperature of ionic liquids is proposed. As known, the values of physicochemical properties of compounds having either homologous cations or anions follow a regular smooth pattern, a characteristic that can help in determining the presence of outliers in a set of experimental data. This characteristic of regular smooth pattern also facilitates the calculation of properties of a given substance by knowing the same property for another substance that has the same cation or anion. A selected database of melting temperature data of ionic liquids available in the literature was constructed and used for determining the melting temperature of those substances for which homology was possible to be applied. The results show that the values determined for the normal melting temperature are accurate enough for engineering calculations and that the melting temperature can be predicted with average uncertainty similar to some experimental data.

1. Introduction

The special properties of ionic liquids (ILs), such as very low vapor pressure, large liquidus range, high thermal stability, high ionic conductivity, and large electrochemical window, among others, make these fluids of special interest for several applications. Additionally, since thousand of combinations between cations and anions can be done, ionic liquids can be designed for almost any specific use [1]. Although the first room temperature ionic liquid was discovered more than a century ago, it has been during the last 20 years that these extraordinary fluids have attracted the attention of the scientific community [2].

Current studies on ionic liquids cover a variety of subjects such as electrochemistry, separation science, chemical synthesis, catalysis and pharmaceuticals, The use of ILs as thermal fluids, lubricants, catalysts and solvents, and their application to biomass processing, biphasic chemical processes, photovoltaic cells, fuel cell electrolytes, synthesis of inorganic nanomaterials, extraction of organic compounds, enzymatic reactions, separation of inorganic materials, and many others, are being continuously discussed in the literature and new advances appear every day [3–9]. Classic books such as those of Wypych [10], Wasserscheid and Welton [11] and Koel [12] contain abundant information about properties, uses and applications of ionic liquids. Also of the many recent papers describing the multiple applications of ionic liquids the recent review of Giernoth [13] provides an overview of the wide variety of applications of ILs beyond their use as solvents and discusses the task-specific characteristic of ionic liquids. Also, Aparicio et al. [14] present a good account on thermophysical properties of pure ionic liquids. These authors analyze the type of thermophysical properties data

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Notation

Symbols

R^2	Coefficient of determination
T_m	Melting temperature
$\%\Delta T_m$	% deviation between correlated and experimental melting temperature
$\lvert\%\Delta T_m\rvert$	Absolute % deviation between correlated and experimental melting temperature
T_m^{cal}	Calculated melting temperature
$T_m^{\exp}$	Experimental melting temperature
[X][Y]	Ionic liquids having [X] as the cation and [Y] as the anion

Abbreviations

IL, ILs	Ionic liquid and ionic liquids
T_m [X][Y]	Melting temperature of ionic liquid [X][Y]

for ionic liquids available in the open literature and the importance of such properties for industrial purposes.

From the industrial point of view, a fundamental understanding of the chemical, physical and thermodynamic properties of ILs should be known before their optimum industrial application. For instance, knowledge of some basic properties is useful in the area of fluid property estimation, thermodynamic property calculations, and phase equilibrium, among others. Several correlations for the density or the heat capacity make use of the critical properties, correlations for the viscosity make use of the density, vapor pressure correlations make use of heat of vaporization, and sublimation pressures make use of melting temperature [15]. This last property, the melting temperature, is of interest in this article.

The melting temperature (T_m) of organic and inorganic substances is a fundamental physical property and has found wide use in chemical identification, purification, and the calculation of other physicochemical properties. In the absence of experimental data, the melting point has to be estimated [16]. Several empirical and semi empirical methods have been used to predict the normal melting point. Among these, group contribution method and neural networks have been employed [16–20]. Although these represent important approaches that should continue being discussed at present there is no general method applicable to any fluid. On the one hand, for neural network applications one needs a reasonable amount of data and a clear picture of the influence of certain properties on that one of interest. In some cases, both requirements are not fulfilled for ionic liquids. On the other hand, group contribution methods were developed for simple substances, mainly hydrocarbons, and its extension to predict properties of ionic liquids is not clear yet. It seems that the way in which molecules are broken into groups is quite different in ionic liquids and most probably the equations that define a property in the group contribution method must be reformulated [21]. Computer simulation and computational chemistry have also been employed and some few applications have been published [22,23].

The concept of homologous series has also been used to correlate melting point data of organic compounds, but still the method is of limiting applicability due to the form in which it has been applied and also due to other inherent limitations as discussed later in this paper [24]. Zhao and Yalkowsky [16] applied a combined approach of group contribution and nonadditive molecular parameters to estimate the melting points of aliphatic compounds. In that study, a similar combined approach is applied to predict the melting points for a database of more complex organic compounds [25].

For ionic liquids, very little progress has been made and very few methods have been used for the estimation of melting points. Katritzky et al. [26] discussed a variety of melting point correlation and prediction methods. In particular they analyzed the capabilities of the CODESSA program (Quantitative Structure/Activity Relationships) for correlating the melting points of imidazolium bromides and benzimidazolium bromides. The descriptors they used for describing these types of ionic liquids were based on the size and electrostatic interactions in the cations. Similar studies have been presented by several other authors [27–30], used a recursive neural network (RNN) to predict the melting points of several pyridinium-based ionic liquids (ILs). According to the authors, the adopted representation of molecular structures captures some significant topological aspects and chemical functionalities of the IL molecules. Huo et al. [31] presented a group contribution method for predicting melting points of imidazolium and benzimidazolium ionic liquids. More recently, Preiss et al. [32] calculated the melting points of crystalline ionic liquids from the ratio of the fusion enthalpy and entropy at the melting point where solid and liquid phases are in equilibrium. The method relies on simple calculations feasible with standard quantum chemical program codes.

2. Melting temperature

Melting happens when the molecules or ions fall out of their crystal structures, and become disordered liquid. This should not be confused with glass transition which is the change that happens from solid state to amorphous solid, but even crystalline solids may have some amorphous portion. This is why the same sample of ILs may have both a glass transition temperature and a melting temperature. Freezing point has the same meaning as melting point but an opposite process [2]. The melting process of ILs is governed by van der Waals forces and electrostatic interaction forces, and the impact of the two forces plays different roles for different kinds of ILs [33].

The liquidus ranges exhibited by ionic liquids can be much greater that those found in common molecular solvents. These ranges go from the melting or glass transition temperature to the decomposition temperature, which is usually before vaporization. Water, for example, at 1 atm. has a liquidus range of 100 °C (0 to 100 °C),