New quantum chemistry-based descriptors for better prediction of melting point and viscosity of ionic liquids

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A B S T R A C T

Ionic liquids (ILs) are chemicals that are nonvolatile and hence have the potential to replace volatile organic compounds in industrial applications. A large number of ILs, through the combination of different cations and anions, can potentially be synthesized. In this context, it will be useful to intelligently design customized ILs through computer-aided methods. Practical limitations dictate that any successful attempt to design new ILs for industrial applications requires the ability to accurately predict their melting point and viscosity as experimental data will not be available for the designed structures. In this paper, we present two new correlations for precise prediction of melting point and viscosity of ILs solely based on inputs from quantum chemistry calculations (no experimental data or simulation results are needed). To develop these correlations we utilized data related to size, shape, and electrostatic properties of cations and anions that constitutes ILs. In this work, new descriptors such as dielectric energy of cations and anions as well as the values predicted by an 'ad-hoc' model for the radii of cations and anions (instead of their van der waals radii) were used. A large number of correlation equations consisting different combination of descriptors (as inputs to the model) were tested and the best correlation for viscosity and melting point were identified. The average relative errors were estimated as 3.16% and 6.45% for melting point, T_m, and ln(vis), respectively.

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1. Introduction

Ionic liquids (ILs) are group of chemicals that have very interesting properties such as negligible vapor pressure, high thermal stability, wide electrochemical window, and high solvency power. The aforementioned characteristics make them promising candidates for multitude of applications. Ionic liquids are mainly composed of large organic cations and organic or inorganic anions. Physical properties of ionic liquids can significantly vary from their sister compounds, ionic salts. The properties of ionic salts can be completely and solely attributed to their ionic nature since strong ionic bonds hold their particles together. Ionic salts are mostly made up of small monoatomic ions, with similar size and shape, within the close vicinity of one another in their lattice crystal network. The lattice energy of crystalline compounds is proportional to the inverse of the distance between their lattice points. The ionic bonds in salts are very strong due to the relatively short distance between the small ions contributing to their high melting

point values. On the contrary, ionic liquids are made up of large multi-atomic cations and anions resulting in weaker ionic bonds. This explains the considerably low melting point and viscosity of ionic liquids compared to those of ionic salts. The multi-atomic nature of cations and anions in ionic liquids presents a great opportunity to fine tune their properties with an aim to cutomize them for different applications. In ILs, cations, and occasionally anions, are composed of side chains with alkyl groups (CH_2, CH_3, etc.) and/or functional groups (OH, NH_2, COOH, etc.) making it possible to functionalize ionic liquids for different applications. A vast number of ILs (estimated to be about 10^{14}) [1] can be potentially synthesized through distinct combinations of different cation-cores, alkyl groups, functional groups, and anions. Careful evaluation of experimental data, from literature, of the physical and thermodynamic properties of ILs shows that substituting functional groups can drastically alter a property of interest.

Despite the fact that the ionic bonds in ILs are relatively weak, their properties can still be attributed to their ionic nature as even a weak ionic bond is still stronger than any other type of intermolecular forces. Crystal network of ionic materials (e.g. ionic liquids) are made of cations and anions held together by electrostatic attraction. The ionic force between charged particles is directly

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proportional to the charge of each particle and inversely proportional to the distance between them. Larger the cations and anions are, weaker the ionic bonds between them will be. This is due to the fact that larger the distance between two ions lower is the electrostatic attraction which holds them together.

Computer-aided optimization methods can help in designing optimal ionic liquids suitable for different applications from solvent extraction to thermal energy storage [2,3]. ILs are generally salts that are in liquid phase below an arbitrary temperature, commonly 100 °C. Therefore, several ILs are in solid state at room temperature. When it comes to the melting point of ILs, those with significantly lower melting points or "room temperature ionic liquids [RTILs]" (T_m < 25 °C), are of great interest to researchers seeking new industrial applications. One main reason for the desirability of low melting point of ILs is the fact that they can be used as solvents (or absorbents) for separation tasks involving selective dissolution of solutes in gas (e.g. CO_2), liquid (e.g. toluene), or solid (e.g. cellulose) states. They are also widely considered as liquid solvents to promote chemical reactions [4,5]. From a practical point of view, for an IL to be used as an industrial solvent it needs to be transported (pumped) across multiple unit operations and therefore it must be in the liquid phase.

Another significant barrier towards commercialization of IL-based applications is their high viscous characteristics due to their ionic nature (existence of relatively strong ionic bonds) resulting in transportation difficulties. This necessitates the use of powerful pumping equipment and efficient process equipment to handle viscous fluids. Therefore, identification and customization of ILs that have relatively low viscosity and appropriate melting point will greatly aid in their accelerated discovery and commercialization. Several models exist for prediction of melting point and viscosity of ILs. In general, these models are either Quantitative Structure Property Relationship (QSPR) correlations [6–8], group contribution (GC) type [9–16], or molecular dynamics (MD) simulations [17–23]. The main drawback of the QSPR and GC models is the narrow restrictions in choice of applicable compounds while the main limitation of MD simulations is the high computational demands and the need for starting geometry [24]. In this paper, we present two empirical correlations to predict melting point and viscosity of ILs in a way that does not need experimental input or tedious simulations, but rely on inputs from simple quantum chemical calculations.

2. Methods

Widely available data and research findings related to melting point and viscosity of salts explicitly shows that there is a meaningful relationship between the magnitude of the two properties and the lattice energy of ionic bonds. Generally, in an ionic compound, size (volume and area), shape (sphericity), molecular weight, and dielectric energy of ions, play important roles in determining the strength of an ionic bond. Normally, larger size of cations and anions, result in longer distances between these ions in the crystal lattice, making the ionic bond weaker. On the other hand, the shape of the ions is also important as they are better packed together when they are symmetrical in nature. It has been suggested that asymmetry of ions in an ionic compound, most likely, will decrease the melting point since the ions are more loosely connected and can be easily separated from each other (by applying lower amount of energy). Therefore we focused on using size, shape, and electrostatic properties to develop new correlations for the prediction of ILs' melting points and viscosities. When we studied the size of cations and anions of a wide variety of ionic liquids and compared with their melting points and viscosities, we found that there were several ILs that violated these general trends,

i.e. ILs with relatively large cations and anions did not necessarily have low melting point or viscosity. One reason could be that in ionic liquids, ionic bonds are not the only intermolecular forces responsible for holding the particles together and other types of forces such as hydrogen bonding and polar-polar forces also come into play. In order to better account for deviations discussed above we included, in addition to the three descriptors size, shape, and electrostatic properties, several other quantum chemical descriptors to refine the correlations to cover a wide variety of ionic liquids. Another challenge was that for several ILs, there were multiple experimental data reported in the literature for these two physical properties. This inconsistency was especially observed in the case of melting points which could be due to the existence of impurities or different crystal network systems. In this study, we did not include ILs that had inconsistent experimental values, during the development of the correlations. Ionic liquids selected for this study were all 1:1 (one cation and one anion) with delocalized charges. These types of ILs are normally able to avoid crystallization and form glasses compounds far below room temperature [25].

Currently, the most widely used approach to predict the melting point of ILs is quantitative structure-property relationship (QSPR) models, mostly combined with artificial neural networks (ANNs) [25]. In this approach, there is a reasonably good correlation between actual and predicted melting points within a standard deviation of less than 10 °C [25]. The limited availability of experimental data on physical properties of ILs is the main drawback of constructing good QSPR models. In recent years, simulations with molecular dynamics (MD) have evolved to study the behavior of ILs. The quality of these simulations strongly depends on the employed force fields. Several groups have tuned them specifically for ILs, while others have modified previously existing force fields. For example, Alavi and Thompson [25] have used MD simulations to predict the melting temperature of $[C_2MIm][PF_6]$. The demanding simulation indicated a melting point that was approximately 43 °C too high [25].

Quantum chemistry data related to the constituents of the ILs, i.e. cations and anions, were obtained using TURBOMOLE software which is a powerful, general-purpose Quantum Chemistry (QC) program, for ab-initio electronic structure calculations [26]. This software allows for accurate prediction of cluster structures, conformational energies, excited states, and dipoles that can be utilized for different purposes. When a chemical compound, in our case a cation or an anion, is simulated using TURBOMOLE, it can be exported as a Cosmo file, which can be used in COSMOtherm software [26]. COSMOtherm is a universal tool, which combines quantum chemistry (QC) and thermodynamic laws to calculate different properties of chemicals and solvents [27]. This method can estimate the chemical potential of different molecules (in pure or mixed forms) at different temperatures. In contrast to other methods, COSMOtherm can predict thermodynamic properties of compounds as a function of concentration and temperature by equations, which are thermodynamically consistent [27]. In the this study, for all the cations and anions, their corresponding COSMO files were imported from COSMObaseIL database (Version 1501), provided by the Cosmologic Company, in which the compounds geometries are optimized, the ground state energies are calculated, and the corresponding COSMO and gasphase files are generated all using TZVP (BP_TZVP_C30_1501) basis set. In the next step, the computational chemistry information of the selected cations and anions, required for the development of the correlative equations, were collected from their COSMO files. These data were either used directly (without any changes) or as a combination with other data (as the secondary descriptors) as the inputs to the correlative equations utilized to predict the melting point and viscosity of ILs.