



An enhanced group-interaction contribution method for the prediction of glass transition temperature of ionic liquids

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ABSTRACT

The glass transition temperature (T_g) of ionic liquids (ILs) was estimated with a group-interaction contribution method. This temperature is very important for phenomena in polymeric materials, amorphous pharmaceutical solids and semiconductors. The proposed method was applied using the group-interaction contribution approach previously developed by Marrero-Morejón and Pardillo-Fontdevila [1], with some modifications to introduce two-order contributions: firstly, simple interaction contribution and secondly, binary interaction contribution. In this study, a comprehensive set of experimental data for 368 ionic liquids with different molecular structures was used to obtain the predictive model and all interaction contributions for all groups in the ionic liquids, including cation and anion groups. A wide range of Imidazolium, Pyridinium, Triazolium, Sulfonium, Pyrrolidinium, Piperidinium, Phosphonium, Oxazolidinium, Ammonium, Morpholinium, Guanidinium, Amino acids and Caprolactam-based ILs were considered in this study. The results show that, with an average absolute relative deviation (AARD) of 3.08% and a correlation coefficient of 0.96, this method represents an excellent alternative to previous approaches for the estimation of the glass transition temperature of diverse ionic liquids from the knowledge of their molecular structure.

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1. Introduction

Ionic liquids (ILs) are salts that can occur as stable liquids below a threshold temperature (usually around 100 °C). They are also referred to as liquid electrolytes, molten salts, ionic melts, ionic fluids, liquid salts or ionic glasses [2–5]. Ionic liquids consist of a combination of large organic cations with various alkyl substituents and inorganic or organic anions. The number of ILs that can be obtained from cation-anion combinations is estimated at more than a trillion [6]. They represent one of the major attractions of the chemical industry today due to their interesting properties [7] which include: a) extremely low vapour pressure [8,9]; b) low or reduced flammability hazards [10]; c) tunable properties [11]; d) excellent solvation properties for a variety of organic and inorganic compounds [11]; e) high electric conductivities [11]; f) high thermal stability [12]; g) a wide liquid range [13]; and h) a wide electrochemical window [14]. Hence, Plechkova and Seddon [15] have outlined many potential industrial applications of ionic liquids.

Moreover, any desired set of properties can be imparted to an ionic liquid by a proper selection of the anion-cation pair. This tunability of ionic liquids' properties allows a very wide range of applications [11]. Understandably, there is high expectation amongst researchers that ionic liquids will bring unprecedented developments in industrial chemistry as well as chemical technology, while spurring several research fields. However, the lack of relevant information regarding their syntheses, structure and properties is impeding progress in this burgeoning field [16,17]. Consequently, determining and understanding the properties of ionic liquids through experiments and modelling studies is essential for the development of ionic-liquid based processes as well as the design of new ionic liquids for specific applications. One such property is glass transition temperature on which this study is focused.

Glass transition temperature (T_g) is referred to as that corresponding to a gradual and continuous transformation from liquid to glass, quite below the melting point. In other words, a transition from solid state to amorphous solid is observed upon heating at this temperature. Even crystalline solids can exhibit some amorphous behaviour. For this reason, ionic liquids have both a melting temperature and a glass transition temperature [18]. Although glass

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transition occurs over a certain region, a single value is used to report the T_g [19]. Glass transition is accompanied by a significant change of some physical and thermodynamic properties such as effective compressibility, expansivity and electric polarizability as functions of temperature [20].

The temperature-dependence of diffusion coefficient, viscosity and conductivity can be estimated using glass transition temperature [21,22]. Furthermore, the potential for ionic liquids to serve as electrolytes in batteries (which is related to diffusion coefficient and conductivity) can be assessed knowing, among other things, the T_g [22]. These well-illustrate the practical importance of the latter thermal property in Science and Engineering.

Experimental methods for glass transition temperature (T_g) measurements include differential scanning calorimetry, cold-storage polarizing microscopy, X-ray scattering and Nuclear Magnetic Raman [23]. In relation to ionic liquids, the quasi-entirety of experimental data reported in the literature for glass transition temperature has been obtained by means of differential scanning calorimetry and differential thermal analysis (DSC/DTA). On a theoretical ground, some researchers have attempted to derive methods to predict the glass transition of ionic liquids using available T_g literature data. In this regard, Lazzús [24] pioneered when he derived a group contribution method for the prediction of the glass transition temperature of ionic liquids. He reported an average absolute relative deviation (AARD) of 5% between predicted and experimental data for 250 ionic liquids. Better model performances (AARD of 1.98% for 73 ILs, 1.38% for 109 ILs and 2.68% for 109 ILs) were reported by Mirkhani et al. [25], Mousavisafavi et al. [26] and Mousavisafavi et al. [27] respectively.

However, their QSPR-based models are applicable to only one specific type of ionic liquids. To cover various types of ionic liquids, another group contribution method was suggested by Gharagheizi et al. [22], demonstrating good agreement with the experimental data of 496 ILs as the AARD was calculated as 3.65%. Predictions by the QSPR model proposed by Mirkhani et al. [23] were also generally consistent (AARD = 3.84%) with literature data associated with 139 ILs. Recently, Yan et al. [28] proposed a new approach of QSPR for T_g prediction which, contrary to all the above similar methods, takes into account anion-cation interactions. The accuracy of this method was found to be higher than that of the aforementioned QSPR methods (AARD = 3.32%). However, the database (139 ILs) used by Yan et al. [28] was smaller than those in previous QSPR studies.

As highlighted in the literature, group contribution methods, although less complex than quantitative structure-property relationship (QSPR), are inaccurate when predicting properties for isomers [1,22]. Group-interaction contribution (GIC) methods were introduced *inter alia* to address this limitation exhibited by conventional group contribution methods [29]. Thus, in the quest for more accurate predictions, a GIC method is proposed in this present study for estimating the glass transition of ionic liquids, similar to the approach proposed by Marrero-Morejón and Pardillo-Fontdevila [1]. Altogether, 368 ILs based on various cations and anions have been used to develop the proposed GIC model.

2. Methodology

2.1. Data set

The database for this study comprised experimental glass transition temperatures (T_g) ranging from 156.15 to 446.25 K, for 368 ionic liquids. All the experimental glass transition temperatures were taken from Zhang et al. [18]. The investigated ionic liquids whose chemical structures are shown in Figs. 1 and 2 consisted of 13 different cation and 22 anion types. Cations included

imidazolium ([IM]), triazolium ([Taz]), guanidinium ([Guan]), pyridinium ([$(R_1R_2)N=(R_3R_4)$]), sulfonium ([S]), pyrrolidinium ([PY]), piperidinium ([PP]), phosphonium ([P]), oxazolidinium ([OX]), ammonium ([N]), morpholinium ([MO]), benzotriazolium ([Bt]) and aminoacids [AA]. Anions contained in the investigated ionic liquids were hexafluorophosphate ([PF₆]), tetrafluoroborate ([BF₄]), bis (trifluoromethylsulfonyl) imide ([BTI]), halide ([X]), alkylsulfate ([R_1SO_4]), carboxylates ([R_1COO]), dialkylphosphate ([R_2PO_4]), trifluoromethylsulfonate ([TfO]), trifluoroacetate ([TfA]), dicyanamide ([dca]), tricyanomethanide ([TCM]), Tris (trifluoromethylsulfonyl) methide ([Tf₃C]), 5-nitrotetrazolate ([Ntet]), 4,5-dinitroimidazolate ([Nlmi]), 3-nitro-1,2,4-triazolate ([Ntri]), azide ([N₃]), perchlorate ([ClO₄]), nitrate ([NO₃]), sulfonate ([R_1SO_3]), borate ([$R_1R_2R_3R_4B$]), sulfonate ([R_1SO_3]), dinitramide ([N(NO₂)₂]).

2.2. Development of the new method

In this study, the molecular structure of a compound is considered to be the collection of three levels of approximation: first-order contribution, second-order contribution and third-order correction contribution. The developed model is based on principles outlined in early works reported in the literature [1,30] as mentioned in these following points:

1. Firstly, the T_g of a compound is considered to be a function of structurally dependent parameters which are thereby determined by summing the number frequency of each simple group-interaction occurring in the molecule, times its contribution between bonding groups instead of the contribution of simple groups, such as $-C-$ & $-N-$. This approach was proposed by Pardillo-Fontdevila and González-Rubio [31] as well as Marrero-Morejón and Pardillo-Fontdevila [1]. These group-interactions can allow the distinction of a large number of isomers. Altogether 80 simple groups were selected to generate a consistent set of group-interactions which allows one to treat various types of ionic liquids. These groups are the same as those used by Marrero-Morejón and Pardillo-Fontdevila [1], with the exception of some specific groups related to various classes of ionic liquids.
2. Secondly, as in the method proposed by Constantinou and Gani [30], the T_g property prediction is performed in three levels of approximation. The basic level uses contributions from first-order simple groups, while the second level uses a small set of second-order groups having the first-order groups as building blocks. This concept is used in this study to avoid the complexity of the property estimation by the integration the multi-order in the model. First-order uses interaction contributions from simple groups (e.g. CH_3- & $-CH_2-$) and interactions between a cation and anion (interactions of single groups $>N<^+Cl$) and second-order uses binary interaction contributions between bonding groups (e.g. $-CN$ & $-N^-$ & $-CN$). The third-order is considered as a correction term. The role of this correction is to consider the distinction of a large number of isomers and the proximity effects.

2.3. Proposed model

Ionic liquids were broken down into groups whose interactions independently contributed to the studied thermal property (i.e. glass transition temperature). Model variables included the sub-structures (groups), their number of occurrences as well as their interactions for each IL. The value associated with the group was defined as 0, when the group did not appear in the IL molecule; and n , when the group appeared n times in the substance. The linear

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