C. R. Chimie 20 (2017) 573–584

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

Glass transition temperature of ionic liquids using molecular descriptors and artificial neural networks

José O. Valderrama [a, d, *], Richard A. Campusano [b, d], Roberto E. Rojas [c]

[a] Faculty of Engineering, Department of Mechanical Engineering, University of La Serena, La Serena, Chile
[b] Faculty of Sciences, Department of Physics and Astronomy, University of La Serena, La Serena, Chile
[c] Faculty of Sciences, Department of Chemistry, University of La Serena, La Serena, Chile
[d] Center for Technological Information (CIT), Monseñor Subercaseaux 667, La Serena, Chile

ARTICLE INFO

Article history:
Received 12 October 2016
Accepted 24 November 2016
Available online 20 February 2017

Keywords:
Ionic liquids
Glass transition temperature
Neural networks
Molecular structure
Molecular descriptors

ABSTRACT

Glass transition temperature data of ionic liquids (ILs) are analyzed to study the capabilities of artificial neural networks to correlate and predict this property. Molecular descriptors from computational chemistry are considered as independent variables to define the characteristics of an IL molecule. Several network architectures were considered, combinations of different descriptors were analyzed, and results were compared with other values reported in the literature. The independent variables (those that could have influence on the glass transition temperature) considered for training the artificial neural networks were (1) mass connectivity index λ, (2) cation mass M(+), (3) anion mass M(−), (4) surface area S_A, (5) van der Waals volume V_w, (6) connectivity index X_0, and (7) number of carbon atoms nC. The mass connectivity index is a parameter previously defined by the authors and is calculated for each IL, whereas the descriptors S_A, V_w, X_0, and nC were determined using the software Dragon7. As a measure of the accuracy of the method, the average relative deviation and the average relative absolute deviation are evaluated. Results of this work and others indicate that appropriate selection of data, good combination of architecture, and variables can lead to acceptable correlation of data but accurate prediction is not yet possible. The lack of a clear definition of the glass transition temperature and the lack of knowledge on what are the properties that most affect liquid–solid transition are the main causes of the present incapability for accurately predicting the glass transition temperature of the IL studied in this work.

1. Introduction

Glass transition is the change that happens from solid state to amorphous solid and knowing the temperature at which this change occurs is of interest in various applications: (1) diffusion coefficient conductivity are related to T_g [1]; (2) T_g can be used to predict the dependence of viscosity on temperature [2]; (3) T_g also serves as a cohesive energy parameter [3]; (4) T_g is one of the main criteria for the evaluation of the potential options for electrolyte applications [4]; and (5) T_g is important for phenomena in polymeric materials, amorphous pharmaceutical solids, and semiconductors [5].

Data of glass transition temperature for some ionic liquids (ILs) are available in the literature and databases such as ILs' database of the IUPAC [6], Beilstein database [7], Dortmund Data Bank [8], or the compilation by Zhang et al. [9] are available. An estimate from these sources indicates that there must be around 900 values of T_g for around 800 ILs. The total amount of data is greater than the amount of

* Corresponding author. University of La Serena, Faculty of Engineering, Department of Mechanical Engineering, Box 554, La Serena, Chile.
E-mail address: jvalderr@userena.cl (J.O. Valderrama).

http://dx.doi.org/10.1016/j.crci.2016.11.009
1631-0748/

ILs because for some ILs several values, reported by different researchers, are available.

Glass transition does not occur at a specified fixed temperature, commonly denoted as T_g, but in a range of temperature or transition region [10]. However, the assignation of a single value for T_g is the common practice found in the literature for this property. In differential scanning calorimetry experiments (DSC), the usual way to determine this property is that T_g is commonly assigned to the onset point, intersection of the initial straight line and the transition region straight line, or to the midpoint of the transition region (inflection point). In this study, the highest value provided in the literature for T_g was considered as the true value. This is because the main uses of ILs are those in which the phase remains as liquid. Crystal formation or solidification is to be avoided in most applications of ILs. Therefore, by selecting or estimating a higher value for T_g the range of applicability of the IL is reduced but one can assure that crystal formation or solidification is to be avoided in most applications of ILs.

Schmelzer et al. [11] present a detailed discussion about the glass transition phenomenon and the glass transition temperature, but it is mainly dedicated to the vitreous state of glasses and not to ILs. However, the phenomenon is similar and the fundamentals are also analogous. According to the authors, "*the notation glass transformation (or glass transition) temperature, proposed by Tammann, is to some extent misleading. Correct with respect to the indicated mechanism of vitrification is the proposal developed by Simon, to denote T_g as the freezing-in temperature of the glass*". In the physics of high polymers, the name temperature of vitrification is preferred and more precisely corresponds to the word Glastemperatur used in the German literature. In the area of IL research the name *glass transition temperature* has been preferred.

Gómez et al. [12] present a thorough analysis of the thermal behavior of pure ILs and define some of the characteristic temperatures that appear during the transition between liquid and solid (or vice versa) of an IL: melting temperature (T_m), freezing temperature (T_f), cold crystallization temperature (T_{cc}), solid–solid transition (T_{ss}), and glass transition temperature (T_g). They define the glass transition temperature T_g "*as the midpoint of a small heat capacity change upon heating from the amorphous glass state to a liquid state*". However, not all authors use this definition and different values for the same IL are proposed in the literature.

The solid–liquid transition temperatures of ILs are usually less than ambient temperature and can go less than −100 °C, such as in the cases of [C2mim][dca] or [C4mim][C2F5BF3] [13]. As mentioned above, the most common and efficient method for experimentally determining T_g is by DSC. The thermal behavior of ILs can be relatively complex and some peculiar and particular characteristics have been observed when cooling or heating an IL [12–14]: (1) the cooling from the liquid state may cause glass formation at low temperatures; (2) solidification kinetics is commonly slow; (3) on cooling from the liquid, the low-temperature region is not usually bounded by the phase diagram liquid line; (4) formation of metastable glasses may occur; (5) heating from the glassy state yields an exothermic transition associated with sample crystallization, followed by subsequent melting; and (6) multiple solid–solid transitions (crystal–crystal polymorphism or plastic crystal phases) may occur. The authors also provided a couple of important recommendations: (1) thermodynamic data should be collected in heating mode to obtain reproducible results; and (2) to obtain reliable transition data, long equilibration times should be allowed and small samples should be taken, to permit rapid cooling. In addition, Gómez et al. [12] state that it is not always possible to correctly identify the different transitions appearing in a thermogram using DSC and additional techniques should be included (crossed polarizing filters, X-ray diffraction, and infrared spectrometry). The authors also state that it is necessary to subject the IL to different heating and cooling rates to have a better interpretation of the thermograms and to define characteristic temperatures such as melting or glass transition. It is not unusual to have ILs with different structures presenting the same thermal behavior and ILs with similar structures presenting different behavior.

These facts may explain the great differences found in reported experimental data of T_g for the same IL. As shown in Table 1 differences up to 38 °C (20%) are found, such as the case of 1-butyl-3-methylimidazolium trifluoroacetate. Other ILs present lower differences but still of importance for modeling and analysis. For butylammonium formate the difference is 25 °C (16%) and for 1-ethyl-3-methylimidazolium-bis[(trifluoromethyl)sulfonyl]imide the difference is 20 °C (11%).

2. Models for T_g presented in the literature

Despite the differences between T_g data such as those shown in Table 1, some proposals have been presented in the literature for correlating and estimating the glass transition temperature. Mirkhani et al. [16] studiedquantitative structure property relationship (QSPR) models for the glass transition temperature of different types of ILs. They claim that a simple predictive model is obtained. Although the absolute average deviation was low (3.8%), deviations more than 10% were found for 10 of the 139 fluids considered in the study. Better results were obtained when the authors considered a specific type of IL such as ammonium-based ILs. In that case, average absolute deviation was 2% and maximum deviations were less than 10%.

Gharagheizi et al. [17] presented a group contribution method to correlate and predict the glass transition temperature of ILs but only for 1,3-dialkylimidazolium–type ILs. For the 190 ILs considered in the study, the authors found an average absolute deviation of 1.9% with maximum deviations of 8.2%. Mousavisafavi et al. [4] also studied the same type of ILs and the same 109 data points using a linear QSPR method and obtained average absolute deviations on the order of 2.7% and maximum deviations of 8.8%. The same group of researchers [18] proposed a nonlinear approach of the QSPR method for obtaining a model that gives average absolute deviation of 1.4% and maximum deviation of 6.7% for the same data set.

Yan et al. [19] also used the QSPR methodology using topological indexes defined by the authors. The QSPR