A new group-interaction contribution method to predict the thermal decomposition temperature of ionic liquids

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ABSTRACT

In this study, a new approach based on group-interaction contribution (GIC) is proposed for predicting the thermal decomposition temperature (T_d) of ionic liquids (ILs). It was developed using a large database which consisted of 639 experimental data points associated with a wide variety of cations and anions. The whole dataset was split randomly into a training set having 499 data points and a validation set with 140 data points. From average absolute relative deviation (%AARD) and correlation coefficient (R^2) values calculated as 4.22% and 0.866 respectively, it was concluded that the model was accurate enough for reliable predictions. More importantly, the new model accounts for isomers distinguishing, which represents an advantage over the conventional group contribution methods reported in the literature.

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1. Introduction

Environmental and safety concerns have prompted an active quest for "green" alternatives to molecular solvents currently used in industrial chemical process. In recent years, ionic liquids (ILs) have been identified as potentially good replacements for conventional solvents [1]. These compounds are defined as molten salts that exist as liquids at temperatures as low as 100 °C [1]. They attracted attention from the academic and industrial spheres, due to the following advantageous properties: (i) Extremely low vapor pressure [2,3]; (ii) Low or reduced flammability hazards [4]; (iii) Tunable properties [5]; (iv) Excellent solvation properties for a variety of organic and inorganic compounds [5]; (v) High electric conductivities [6]; (vi) High thermal stability [7]; (vii) Wide liquid range [8]; (viii) Wide electrochemical window [9].

Though ILs are generally regarded as safe and environmentally friendly solvents, some of them are either flammable or volatile [10]. Ions that are present in a given ionic liquid determine its properties [5]. For this reason, desired properties can be imparted to an ionic liquid by a proper selection of the anion-cation combination. The wide range of applications for ionic liquids is owed to this tunability of properties. The design of chemical process as well as products based on ILs require the availability of thermophysical and transport properties of these compounds, determined via experiments or modelling.

In the present study, a model for estimating the thermal decomposition temperature (T_d) of ionic liquids is proposed. The model is based on group–interaction contributions (GIC), and was developed using a large

database consisting of 639 ionic liquids. The thermal decomposition temperature is defined as the upper limit of the liquid us range, the lower limit being the melting point. The liquid us range determines conditions under which an ionic liquid can be used as solvent in chemical processes.

A survey of the literature revealed four significant publications [11–14] related to predictive methods for the thermal decomposition temperature of ionic liquids, based on either group contribution (GC) or QSPR methods. Table 1 summarizes the major features of these models. It can be observed that all the proposed approaches compare favorably with each other in terms of correlation coefficients (R^2) and average absolute relative deviations (%AARD).

It is worth noting that group-interaction contribution (GIC) methods were derived to address the major limitation of conventional methods, i.e. inability to distinguish between isomers. The model presented in this study is similar to that proposed by Marrero and Pardillo [15]. They covered diverse ionic liquids and were generally found to be fairly consistent with experimental thermal decomposition temperatures reported in the literature. Nevertheless, the quest for more accurate predictions and the need to include additional ionic liquids that were not considered in previous studies motivated the present modelling approach.

2. Methodology

2.1. Data set

Experimental thermal decomposition temperature compiled by Zhang and al. [16–17] were used to develop the GIC-based model presented in this study. The database initially consisted of 805 ionic liquids

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Table 1
Predictive models for T_d proposed in the literature.

References	Yan et al. [11]	Lazzús [12]	Gharagheizi et al. [13]	Gharagheizi et al. [14]
Approach	QSPR	GC	QSPR	GC
No of ILs	158	198	586	613
ILs in the training set	126	120	467	489
ILs in the validation set	32	78	119	124
No of functional groups/parameters	25	58	12	30
Optimisation Method	–	GA	GA	Least square
R^2	0.893	0.936	0.832	0.852
%AARD	3.07	4.28	5.18	4.43

whose thermal decomposition temperature were in the range from 350.15 K to 739.15 K. Since some ionic liquids were associated with more than one source of experimental data. In the absence of any recommended standard procedure for T_d measurements, no action was taken to identify erroneous data that would eventually be excluded from the database. Hence, 639 reported data for thermal decomposition temperature points were considered when developing the new model. The ionic liquids considered in the present study covered a diversity of structures which are shown in Fig. 1. Altogether, there were 17 cation types represented. Cations included are Imidazolium ([IM]), Triazolium ([Taz]), Tetrazolium([Tetaz]), Pyridinium([py]), Pyrimidine([$(R_1R_2)N = (R_3R_4)$]), Guanidinium ([Guan]), Sulfonium ([S]), Pyrrolidinium ([Pn_1n_2]), Piperidinium ([PP]), Phosphonium ([P]), Oxazolidinium ([OX]), Ammonium ([N]), Morpholinium ([MO]),Caprolactam([NHC]),Butyrolactam([PY]), Benzotriazolium ([Bt]) and Amino Acids ([AA]). Anions contained in the investigated ionic liquids are Hexafluorophosphate ([PF_6]), Tetrafluoroborate ([BF_4]), 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 ([Tf_3C]), 5-nitrotetrazolate ([Ntet]), 4,5-dinitroimidazolate ([Nlmi]), 3-nitro-1,2,4-triazolate ([Ntri]), Azide ([N_3]), Perchlorate ([ClO_4]), Nitrate([NO_3]), Sulfonate ([R_1SO_3]), Borate ([$R_1R_2R_3R_4B$]), Sulfonate ([R_1SO_3]), Dinitramide ([$N(NO_2)_2$]).

The relative number of cations and involved in the database is provided in Table 2. It can be stated that Td measurements reported in the literature mostly cover Imidazolium, Ammonium, Phosphonium, Piperidinium, Pyrrolidinium-based ionic liquids. These are in fact the most commercially available classes of ionic liquids.

2.2. Method proposed in this work

In order to relate molecular structure to the thermal decomposition temperature of ionic liquids, the proposed model relies on a three-level approximation: first-order contribution, second-order contribution and third-order correction contribution. This was done according to principles outlined in previous works by Marrero and Pardillo [15] as well as Constantinou and Gani [18]. The method suggested by these researchers is articulated around the following three points:

i. the thermal decomposition temperature of a compound is regarded as a function of structurally-dependent parameters, determined as the sum of 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. This approach was proposed by Pardillo and Gonzalez-Rubio [19] as well as Marrero and Pardillo [15]. As pointed out in the literature, the major merit of this approach is to allow for the distinction of a large number of isomers. Conventional group contribution method does not distinguish between isomers. Various simple groups were selected to form a set of group-interactions allowing T_d prediction

for a wide range of ionic liquids, in terms of a variety of cations and anions. The groups selected in this study are similar to those used by Marrero and Pardillo [15]. However, additional groups have been added to take into account specific structural features of ionic liquids.

ii. As in the approach suggested by Constantinou and Gani [18], three levels of approximation are involved in the T_d prediction procedure. The first (basic) level uses contributions from first order-simple groups. A rather small set of second-order groups is used. These have the first-order groups as building blocks. This concept was adopted in this study to avoid the complexity of the property estimation which would be engendered by the incorporation of a multi-order approach. As illustrated in Fig. 2, the first order is associated with interaction contributions from simple groups (e.g.: CH_3— and —CH_2—) and interactions between a cation and anion (e.g.: interactions of single groups $>N<^+$ and Cl^-) and the second order uses binary interaction contributions between bonding groups (e.g.: —CN & —N^-— & —CN). The third-order is a correction term incorporating the equivalent number denoted as E.

iii. Regarding the correction term, three situations are distinct at this stage; the equivalent number (E) where: E = |n_cation × n_anion|, |, n_cation and n_anion are the number oxidation for cation and anion respectively; such as in 1-methylimidazolium bromide ([C1Im]Br), the equivalent number E equals 1, in N,N,N′,N′-tetramethyl-N,N′-dibutyl-1,3-propanediammonium di [bis (trifluoromethanesulfonyl) amide] [$C_3(N_{114})_2$][NTf_2]$_2$ equals 2, and in Tris [2-(oxoethyl(trimethylammonium)ethoxy) triazine tri(nitrate) [$(N_{111},C_2O)_3$triaz][NO_3]$_3$ equals 3. 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 thermal decomposition temperature which was the property of interest. Variables considered in the model consisted of the sub-structures (groups), their number of occurrences as well as their interactions for each investigated ionic liquid. The number of groups represented in an ionic liquid was defined as: 0, when the group did not appear in the IL molecule; and n, when the group appeared n times. As shown in the literature [16,18], a property denoted T_d can be modelled via GIC by means of the following linear correlations:

$$T_d(K) = A + \sum_j n_j \Delta C_j + \sum_k m_k \Delta D_k + f_E E \tag{1}$$

where n_j and m_k are the number of first and second-order groups of type j and k in the molecule respectively and ΔC, ΔD are the group-interaction contributions for the first and second order respectively; E is the equivalent number; and A and f_E are adjustable model parameters. We generated two disjointed subsets by randomly excluding 140 compounds from the entire data set of 499 compounds. The largest subset was used as a training set for fitting the equations presented in Eq. (1) and determining the contributions of both first and second -order groups interactions. The following objective function was used in this study during regression analysis:

$$F = \sum_{i=1}^{n} \left(T_{d_i}^{Exp} - T_{d_i}^{cal} \right)^2 \tag{2}$$

The average absolute deviation (*AAD*), the percent average relative deviation (*%AARD*) and the correlation coefficient (R^2) were calculated