

Melting-Point Estimation of Ionic Liquids by a Group Contribution Method

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Abstract Based on experimental data collected from the literature, a group contribution method for estimating the melting points of imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, phosphonium-, and piperidinium-based ionic liquids (ILs) with common anions is proposed. The method considers the contributions of ionic groups and methylene groups, as additive parameters, and two nonadditive characteristic geometric parameters of cations such as symmetry and flexibility. A total of 293 data points for 136 ILs were used in this study. The average relative deviation and the average absolute deviation of the proposed model are 7.8 % and 22.6 K, respectively. It is concluded that the proposal is useful for the prediction of the melting points for a wide range of ILs.

Keywords Ionic liquids · Melting point · Group contribution · Property estimation

List of Symbols

Cations

$[C_n\text{mim}]^+$ *n*-Alkyl-3-methylimidazolium cation
 $[C_n\text{eim}]^+$ *n*-Alkyl-3-ethylimidazolium cation

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$[C_n\text{pim}]^+$	<i>n</i> -Alkyl-3-propylimidazolium cation
$[C_n\text{bim}]^+$	<i>n</i> -Alkyl-3-butyylimidazolium cation
$[C_{n_1}C_{n_2}\text{im}]^+$	<i>n</i> -Alkyl-3- <i>n</i> -alkylimidazolium cation
C_{n_1} and C_{n_2}	C_1 =methyl, C_2 =ethyl, C_3 =propyl, C_4 =butyl, C_5 =pentyl, C_6 =hexyl, C_7 =heptyl, C_8 =octyl
$[C_n\text{mmim}]^+$	<i>n</i> -Alkyl-2,3-dimethylimidazolium cation
$[C_n\text{py}]^+$	<i>n</i> -Alkyl pyridinium cation
$[C_n(\text{dmN})\text{py}]^+$	<i>n</i> -Alkyl-4-(dimethylamino)pyridinium cation
$[C_n\text{mpyr}]^+$	<i>n</i> -Alkyl-1-methylpyrrolidinium cation
$[C_n\text{mpip}]^+$	<i>n</i> -Alkyl-1-methylpiperidinium cation
$[\text{Am}(n,n,n,n)]^+$	<i>n,n,n,n</i> -Tetraalkylammonium cation
$[n,n,n,n(\text{Ph})]^+$	<i>n,n,n,n</i> -Tetraalkylphosphonium cation

Anions

$[\text{PF}_6]^-$	Hexafluorophosphate
$[\text{BF}_4]^-$	Tetrafluoroborate
$[\text{Tf}_2\text{N}]^-$	Bis(trifluoromethylsulfonyl)imide
$[\text{Cl}]^-$	Chloride
$[\text{CH}_3\text{COO}]^-$	Acetate
$[\text{MeSO}_4]^-$	Methyl sulfate
$[\text{EtSO}_4]^-$	Ethyl sulfate
$[\text{CF}_3\text{SO}_3]^-$	Trifluoromethanesulfonate
$[\text{Pf}_2\text{N}]^-$	Bis(perfluoroethylsulfonyl)imide
$[\text{CF}_3\text{COO}]^-$	Trifluoroacetate
$[\text{N}(\text{CN})_2]^-$	Dicyanamide
$[\text{C}(\text{CN})_3]^-$	Tricyanomethanide
$[\text{AlCl}_4]^-$	Tetrachloroaluminate
$[\text{Br}]^-$	Bromide

1 Introduction

Ionic liquids (ILs) are a class of novel solvents with very interesting properties. They are receiving considerable attention due to their potential uses in synthesis, separations, catalysis, electrochemistry, and much more [1,2]. ILs have a wide liquid range, which, together with their low melting points and the possibility of tuning their physical and chemical properties, offer opportunities for control over reactivity unobtainable with molecular solvents [3].

Many different ILs can be generated by the combination of their cations and anions. Since, their physical and chemical properties can be fine-tuned by combinations of their ions, or by modifying the chemical structures of the constituent ions, they can be tailored to specific tasks [4]. However, the number of possible combinations of cations and anions is around 10^{18} ILs according to Seddon [5]. The experimental work to synthesize all of these ILs and measure their properties is considerable and not feasible. Trial-and-error syntheses should be avoided to minimize costs, labor, and time.

To incorporate this new kind of solvent into industrial applications, knowledge of their physical and chemical properties is essential for their full potential applications. The development of methods to predict the physical properties of unknown ILs before their synthesis is essential and will assist the design and selection of new ILs with desired properties for a specific task.

The normal melting point is one of the most important properties to be considered for the design and application of ILs. In contrast to available melting-point data for organic compounds, melting-point data for ILs is scarce. The wide liquid range shown by ILs is determined by their low melting points governed by the structure and interactions between the ions, as well as their high decomposition points [3]. The melting point of a compound is difficult to correlate, because it is dependent upon the arrangement of the molecules in the crystal lattice, as well as upon the strength of the pairwise group interactions [6].

Even though the development of the structure–melting point relationship is not as straightforward as it is for other properties [7], group contribution methods (GCM) for predicting melting points of organic compounds (non-ILs) have been developed [8–13]. The group contribution approach is a correlation between a property of a compound and an additive function of the group contribution parameters which describe the molecular structure. GCMs for property prediction of ILs have been developed [14–16], but they do not include melting points.

A method currently used to estimate the melting points of ILs is the quantitative structure–property relationship (QSPR) [4, 17, 18]. Another method based on thermodynamic considerations using computer calculations from quantum chemical and COSMO-RS programs for predicting melting points of ILs was reported by Preiss et al. [19]. Recently, a model based on group contributions for estimating melting points of imidazolium and benzimidazolium ILs was developed by Huo et al. [20]. However, this model only considers imidazolium-based ILs.

The objective of this study is to develop a group contribution model for predicting melting points of ILs that include most of the common cations and anions in ILs. The second objective is to extend the set of properties presented by Gardas and Coutinho [14–16]. Accordingly, similar IL groups have been used. To develop the model, we focused our attention on the thermodynamic concepts and experimental data trends of ILs. We present a method for estimating the melting points of ILs, which combines the group contribution (additive parameters) and simple geometric parameters of cations (non-additive parameters).

2 Melting Point

The melting point of a compound represents the lower limit of the liquid range and together with thermal stability defines the temperature window in which it can be used as a solvent [21]. The structure of an IL directly impacts upon its properties, in particular, the melting point and the liquidus range. The liquidus range exhibited by ILs can be much greater than that of common molecular solvents [3]. There is insufficient understanding of the relationship between the melting point of a compound and its chemical structure [22].

The factors that primarily control the melting point of a compound are intermolecular forces, molecular symmetry, and the conformational degrees of freedom of a molecule [6]. For ILs, charge, size, and the distribution of charge on the constituent ions also influence the melting point. Furthermore, within the same class of ILs, small changes in the shape of the uncharged, covalent regions of the ions can also influence the melting point of the salts.

Coulombic interactions, hydrogen bonding, and van der Waals interactions such as dispersion forces are important in the formation of an IL crystalline lattice. The Coulombic energy contributes to the lattice energy of ionic solids through its dependence on (i) the product of the net ion charges, (ii) ion–ion separation, and (iii) packing efficiency of the ions [3]. Besides being affected by charge and size, the melting point of imidazolium ILs is affected by the following factors: electron delocalization, H-bonding ability, the symmetry of the ions, and van der Waals interactions. Both alkyl substitution on the cation and ion asymmetry have been shown to interfere with the packing efficiency of ions in the crystalline lattice [3].

Trends in the melting point with respect to cation structure are observed when melting points are plotted against the cation alkyl chain length. Holbrey and Rogers [3] reported the variation in melting point with alkyl chain length for ILs containing 1-alkyl-3-methylimidazolium cations with several anions. A decrease in the melting point with an increase in the alkyl chain length was observed up to $n = 8$, where n is the number of carbon atoms. For $n > 8$, a gradual increase in the melting point was observed with increasing chain length. Similar trends were observed for the other cations studied in this study.

The asymmetry and the flexibility of the cations, which are entropic factors, contribute to decreasing the melting point of ILs, as was mentioned before. The decrease in the melting point is marked between $n = 1$ and $n = 3$ and less noticeable at longer alkyl chain lengths. However, IL melting points do not continue decreasing beyond $n = 8$; rather an increase in the IL melting point with longer alkyl chains is observed. The addition of methylene groups to a linear hydrocarbon chain increases its van der Waals interaction energy and thus its enthalpy of melting. Van der Waals interactions between the long hydrocarbon chains have the opposite effect to the flexibility term (entropic factor) on the melting point of ILs. Also, replacing the hydrogen atom in the C(2) position of the imidazolium ring by a methyl group generates an increase in the IL melting point. This can be explained by the effect of van der Waals interactions through the methyl group [3].

3 Model Development

The following six cations were considered in this study to establish the model: imidazolium [Im], pyridinium [Py], pyrrolidinium [Pyr], alkyl ammonium [Am], alkyl phosphonium [Ph], and piperidinium [Pip]. Together with these cations, the following 14 anions were considered: hexafluorophosphate $[\text{PF}_6]^-$, tetrafluoroborate $[\text{BF}_4]^-$, bis(trifluoromethylsulfonyl)imide $[\text{Tf}_2\text{N}]^-$, chloride $[\text{Cl}]^-$, acetate $[\text{CH}_3\text{COO}]^-$, methyl sulfate $[\text{MeSO}_4]^-$, ethyl sulfate $[\text{EtSO}_4]^-$, trifluoromethanesulfonate $[\text{CF}_3\text{SO}_3]^-$, bis(perfluoroethylsulfonyl)imide $[\text{Pf}_2\text{N}]^-$, trifluoroacetate

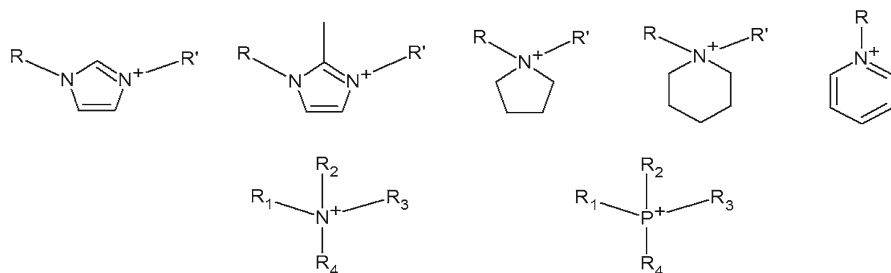


Fig. 1 Building blocks or parent cation groups of ILs studied, where $R = R' = \text{CH}_3$ in heterocyclic rings and $R_1 = R_2 = R_3 = R_4 = \text{CH}_3$ in ammonium and phosphonium

Table 1 Cations of ILs that can be formed from the cation parents in this model

Cation	Number of carbon atoms in alkyl chain
$[\text{C}_{n_1}\text{C}_{n_2}\text{im}]$	$n_1 = 1-8$ and $n_2 = 1-4$
$[\text{C}_n\text{mmim}]$	$n = 1-8$
$[\text{C}_n\text{Py}]$	$n = 1-6$
$[\text{C}_n(\text{dmN})\text{Py}]$	$n = 1-6$
$[\text{C}_n\text{mPyr}]$	$n = 1-6$
$[\text{Am}(n_1), n_2, n_3, n_4]$	$n_1 = 1-8$ and $n_2 = n_3 = n_4 = 1-8$
$[n_1, n_2, n_3, (n_4)\text{Ph}]$	$n_4 = 1-14$ and $n_1 = n_2 = n_3 = 1-6$
$[\text{C}_n\text{mPip}]$	$n = 1-8$

$[\text{CF}_3\text{COO}]^-$, dicyanamide $[\text{N}(\text{CN})_2]^-$, tricyanomethanide $[\text{C}(\text{CN})_3]^-$, tetrachloroaluminate $[\text{AlCl}_4]^-$, and bromide $[\text{Br}]^-$. In this method, ILs can be generated by combining anions and cations. Each of the 14 anions listed above is considered as a group. Cations are generated from the seven cations shown in Fig. 1. These will be called parent cations. Additional cations are formed by adding methylene groups.

In the model developed, the ionic structure of the ILs is considered, to generate the corresponding IL. Besides adding CH_2 groups to the alkyl chain attached to the nitrogen atom of parent cations, it is also possible to extend the range of new ILs. Figure 1 shows the building block cations of ILs (parent cations) considered in this study; these are 1,3-dimethylimidazolium, 1,2,3-trimethylimidazolium, 1,1-dimethylpyrrolidinium, 1,1-dimethylpiperidinium, 1-methylpyridinium, tetramethylammonium, and tetramethylphosphonium. In addition, Table 1 shows all the cations that can be formed from the cation parents for this model. The second column in Table 1 shows the possible combinations considering the alkyl chain length of the cations used in this study.

A cation can be generated from the parent cation by adding methylene groups (CH_2) to the alkyl chain attached to the nitrogen or to the phosphorus atom of the cation. So, it is possible to obtain cations with longer alkyl chains. Therefore, a wide range of ILs can be created combining cations (cation parent, adding methylene groups) and anions. For example, 1-butyl-3-methylimidazolium, $[\text{C}_4\text{mim}]^+$, is composed of one 1,3-dimethylimidazolium (parent cation) plus three CH_2 groups. Thus, to build 1-hexyl-3-methylimidazolium tetrafluoroborate, $[\text{C}_6\text{mim}][\text{BF}_4]$, one 1,3-dimethylimidazolium is needed plus five CH_2 groups and one BF_4^- anion.

Other examples concerning the generation of ILs, starting from their groups are shown below:

For the generation of the following cations:

[C₄Py]⁺, three CH₂ groups plus one 1-methylpyridinium are needed.

[C₄mPyr]⁺, three CH₂ groups plus one 1,1-dimethylpyrrolidinium are needed.

[Am(4)111]⁺, three CH₂ groups plus one tetramethylammonium are needed.

All cations generated above can be combined with the different anions included in this study.

The developed model makes use of the theoretical dependence of the enthalpy and the entropy of melting upon the structure of a compound. The estimation of melting points of organic compounds based on a thermodynamic approach was previously developed by Yalkowsky et al. [12,13,23,24]. When the transition temperature is reached, that is, when the phases are in equilibrium, the free energy of transition is equal to zero. Thereby, the melting point is related to the enthalpy (ΔH_m) and entropy (ΔS_m) of melting by the following relationship:

$$T_m = \frac{\Delta H_m}{\Delta S_m}. \quad (1)$$

These thermodynamic properties, ΔH_m and ΔS_m , show different dependences upon structure. Therefore, to build the model for the melting point, models for the enthalpy and the entropy of melting are considered.

The enthalpy of transition is assumed to be dependent upon the interactions between the molecular fragments and is equal to the summation of the group values. The enthalpy of melting ΔH_m can be therefore calculated by the following relationship:

$$\Delta H_m = \sum n_i m_i \quad (2)$$

In Eq. 2, n_i is the occurrence of the group i in the compound, and m_i is the contribution of the group i to the enthalpy of melting.

The entropy of transition is a measure of the changes in molecular translational, rotational, and conformational freedom that accompany a phase transition. The entropy of melting ΔS_m is mainly determined by the change in rotational and conformational freedom [12].

Dannenfelser et al. [24] found that the change in rotational freedom of a molecule is related to its rotational symmetry number, whereas the change in conformational freedom of a molecule is related to the molecular flexibility number. The estimation of the entropy of melting of organic compounds defined by Dannenfelser et al. [24] was adapted here for ILs to give the following simplified equation:

$$\Delta S_m = a + \sigma_c + c\tau_c \quad (3)$$

where σ_c is a new symmetry parameter defined for the cation, and the parameter τ_c is related to the cation flexibility. The σ_c symmetry parameter is determined by fitting the experimental melting-point values, and τ_c is deduced from a very simple calculation,

such as the number of methylene groups (CH_2) present in the alkyl chain of the cation of the IL minus 1.

Accordingly, the model to estimate the melting point of ILs has been defined as follows:

$$T_m = \frac{\sum_i n_i \Delta T_{m,i}}{a + \sigma_c + c\tau_c} \quad (4)$$

where n_i is the number of groups of type i in the molecule, and $\Delta T_{m,i}$ is the contribution of group i to the melting temperature.

The group contributions (ΔT_m), symmetry of cation (σ_c), and a and c parameters of the model were estimated from a simultaneous optimization of the entire database, minimizing the objective function W described in

$$W = \sum_{i=1}^{N_p} \left[\left(\frac{\sum_i n_i \Delta T_{m,i}}{a + \sigma_c + c\tau_c} - T_{m,\text{lit}} \right)^2 \right]_i \quad (5)$$

Here, N_p represents the number of available data points for all ILs studied, and $T_{m,\text{lit}}$ represents the experimental values of melting points [25–29].

A total of 293 data points for 136 ILs based on imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium, and piperidinium cations with common anions were used in this study.

4 Data Assessment

It is difficult to know the true melting-point value for a particular IL in a set of data reported in the literature from different authors. Usually, experimental data available in the literature show discrepancies in experimental melting-point values. Impurities affect the melting point of a compound. The differences among the melting-point values of an IL could be due to impurities like water and/or halogen ions present in IL samples. Although, the IL can be present in a high purity state, the IL melting point is difficult to define, because the thermal behavior of many ILs is relatively complex. So, Holbrey and Rogers [3] suggest that thermodynamic data should be collected in the heating mode to obtain reproducible results. The dispersion of data reported for example for $[\text{C}_4\text{mim}][\text{PF}_6]$ shown in Table 2 may be due to the level of purity of the samples of the IL or to the method used to determine the melting point.

Experimental melting-point data for ILs found in the literature show differences depending on the sources. For example, the melting point for $[\text{C}_4\text{mpyr}][\text{Tf}_2\text{N}]$ and $[\text{C}_8\text{mim}][\text{Cl}]$ have been reported by different authors. The standard deviation of the data reported and the range between the maximum and minimum values of melting points of both compounds are 6.51 K, 18.60 K and 51.25 K, 94.26 K, respectively. Therefore, before using the melting-point values found in the literature, it is clearly necessary to make a selection of the data to develop the group contribution-based model for the prediction of melting points of ILs.

Table 2 RD of melting points for [C₄mim][PF₆], reported by different authors

<i>T_m</i> (K)	RD (%) Ref. median	
	All data	After deleting data
283.1 [25]	1.81	1.47
276.43 [25]	−0.59	−0.92
277.15 [25]	−0.33	−0.66
284.1 [25]	2.17	1.83
283.1 [25]	1.81	1.47
280.03 [25]	0.70	0.37
279 [26]	0.33	0.00
212.15 [30,31]	−23.71	–
265.15 [27]	−4.65	−4.96
277.15 [27]	−0.33	−0.66
265.15 [27]	−4.65	−4.96
283.15 [27]	1.83	1.49

RD(%) =
 $(T_{m,\text{lit}} - T_{m,\text{median}}) /$
 $T_{m,\text{median}} \times 100$, where $T_{m,\text{lit}}$ is
 the melting point reported in the
 literature and $T_{m,\text{median}}$ is the
 median value of melting points
 in the data set

An exhaustive selection of data points was carried out to develop the predictive model for melting points of ILs. It was found that some experimental melting-point data collected from the literature are very different from a particular set of data for an IL. For example, as will be shown below for [C₄mim][PF₆] in Table 2, the value of 212.15 K [30,31] is distant from the rest. So this value appears to deviate markedly from the other members of the data for specific ILs. Therefore, to eliminate a data point from a set of data, the relative deviation (RD) was calculated for each point using the median as a reference in the set. Table 2 shows the experimental data of melting points reported by different authors [25–27,30,31], and the RD (%), for [C₄mim][PF₆]. It is clear that the data point at 212.15 K has a significant deviation from the median value (278.08 K), and therefore it was eliminated from the set of data.

In this study, the criterion used to select data for melting points was to accept data points in a set of data having a RD (%) <10%, using the median as a reference. Data points with RD (%) >10% were eliminated. After previous selection of those data points, all the other data points found in the literature were included in the multiple regression analysis to find the group contribution, symmetry, and adjustable parameters.

5 Results and Discussion

Table 3 shows the group contribution parameters and the groups of the model for melting points of ILs, while Table 4 shows the estimated value of the symmetry parameter, σ_c of the model for each cation studied. The cation flexibility parameter, τ_c is the sum of the number of methylene (CH₂) groups minus one, of each alkyl chain attached to nitrogen or phosphorus atoms in the respective cation. That is,

$$\tau_c = \sum_k (n(\text{CH}_2)_k - 1) \quad (6)$$

where $n(\text{CH}_2)_k$ is the number of methylene groups in alkyl chain k .

Table 3 Group contribution parameters for melting points of ILs

Species	ΔT_m
<i>Cations</i>	
1,3-Dimethylimidazolium (+)	114.481
1,2,3-Trimethylimidazolium (+)	134.466
1-Methylpyridinium (+)	119.250
1,1-Dimethylpyrrolidinium (+)	137.736
Tetramethyl ammonium (+)	533.952
Tetramethyl phosphonium (+)	572.219
1,1-Dimethylpiperidinium (+)	156.418
<i>Group</i>	
CH ₂	-1.463
Dimethyl amino	37.189
<i>Anions</i>	
PF ₆ ⁻	16.746
BF ₄ ⁻	-0.479
Tf ₂ N ⁻	-0.966
Cl ⁻	35.852
CH ₃ COO ⁻	1.384
MeSO ₄ ⁻	-0.501
EtSO ₄ ⁻	-14.560
CF ₃ SO ₃ ⁻	6.348
Br ⁻	33.219
CF ₃ COO ⁻	-1.809
N(CN) ₂ ⁻	-14.083
C(CN) ₃ ⁻	-3.369
AlCl ₄ ⁻	4.714
Pf ₂ N ⁻	-3.202

Table 4 Assigned symmetry parameter σ_c for each type of cation studied for the model

Type of cation	σ_c Value
R = R' (Im, Pyr, Pip)	0.265
R \neq R' (Im, Pyr, Pip)	0.317
R or R and dimethylamino in C(4) (Py)	0.265
R1 = R2 = R3 = R4 (Am and Ph)	1.301
R1 = R2 = R3 \neq R4 (Am and Ph)	1.532

Table 5 shows some examples of calculated flexibility values τ_c and symmetry parameters σ_c for some cations studied.

The values of the adjustable parameters a and c obtained for the model are 0.100 and 0.012, respectively.

Table 5 Calculated flexibility and assigned symmetry parameters for cations of ILs

IL	τ_c	σ_c
[1,1,1,1Ph][Tf ₂ N]	0	1.301
[4,4,4,14Ph][Cl]	18	1.532
[C ₃ mPip][Tf ₂ N]	1	0.317
[C ₈ mPip][BF ₄]	6	0.317
[Am(1)111][Tf ₂ N]	0	1.301
[Am(6)444][Tf ₂ N]	10	1.532
[Am(1)888][BF ₄]	18	1.532
[Am(8)888][Tf ₂ N]	24	1.301
[C ₁ mpyr][Tf ₂ N]	0	0.265
[C ₅ mpyr][Tf ₂ N]	3	0.317
[C ₆ py][Tf ₂ N]	4	0.265
[C ₄ (dmN)py][Br]	2	0.265
[C ₁ mim][Tf ₂ N]	0	0.265
[C ₆ mim][Tf ₂ N]	4	0.317
[C ₆ mmim][Tf ₂ N]	4	0.317
[C ₁ mmim][Cl]	0	0.265

6 Accuracy of the New Model

The accuracy of the model was checked from an examination of the average relative deviation (*ARD*) and the average absolute deviation (*AAD*). They were determined from Eqs. 7 and 8, respectively, with 293 data points for 136 ILs. The *ARD* of the model is 7.8 %, and the *AAD* is 22.6 K.

$$ARD = 1/N \sum |T_{m,est} - T_{m,lit}| / T_{m,lit} \times 100 \quad (7)$$

$$AAD = 1/N \left(\sum |T_{m,est} - T_{m,lit}| \right) \quad (8)$$

In these equations, *N* is the number of data points, *T*_{m,est} (K) is the estimated melting-point value of an IL, and *T*_{m,lit} (K) is the literature value melting point of an IL.

The relative deviations of the correlation of the melting points of the ILs for the studied cations and anions are shown in Tables 6 and 7. It was observed that ILs based on 1-alkyl-1-methylpiperidinium [C_{*n*}mPip] cations and others based on dicyanamide [N(CN)₂] anions exhibited the highest *ARD* (%). These were 18.20 % and 15.93 %, respectively. Similarly, the *ARD* of ILs composed of 1-alkyl-1-methylpyrrolidinium [C_{*n*}mpyr] cations and others based on tetrafluoroborate [BF₄] anions were also high. The *ARD* were 11.41 % and 12.93 %, respectively.

In particular, experimental data for the melting points of ILs based on piperidinium, ethyl sulfate, tricyanomethanide, and tetrachloroaluminate ions are scarce. So the model was developed using minimal data for these types of IL. It is expected that

Table 6 Average relative deviation of calculated melting points for ILs studied, based on imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, and piperidinium cations

Cation	Temperature range (K)	Data points	ARD (%)
$[C_n C_{n_2} mim]^{+a}$	399.45–190.15	154	6.91
$[C_n mmim]^+$	462.15–235.15	23	6.00
$[C_n py]^+$	378.00–273.00	8	2.33
$[C_n (dmN)py]^+$	495.00–310.00	3	8.45
$[C_n mpyr]^+$	410.10–218.15	30	11.41
$[Am(n)n,n,n]^+$	409.50–230.15	57	9.16
$[C_n mPip]^+$	419.15–273.15	5	18.20
$[n, n, n, (n)Ph]^+$	423.00–286.15	13	6.23

^a With n_2 up to 4

Table 7 Average relative deviation of calculated melting points for ILs based on listed anions

Anion	Temperature range (K)	Data points	ARD (%)
$[Tf_2N]^-$	423.00–233.15	125	8.07
$[BF_4]^-$	419.15–190.15	36	12.93
$[CH_3COO]^-$	354.15–250.15	6	7.61
$[MeSO_4]^-$	308.90–253.15	6	3.64
$[EtSO_4]^-$	236.29	1	0.00
$[CF_3SO_3]^-$	382.15–235.15	18	9.02
$[Br]^-$	495.00–303.15	14	4.58
$[CF_3COO]^-$	332.15–233.15	6	4.21
$[N(CN)_2]^-$	388.15–218.15	10	15.93
$[C(CN)_3]^-$	263.15	1	0.00
$[AlCl_4]^-$	282.15–263.15	3	0.71
$[Pf_2N]^-$	356.15–266.1	5	3.28
$[PF_6]^-$	351.15–212.15	31	6.42
$[Cl]^-$	462.15–264.15	31	3.63

more experimental melting-point data will be available in the literature which could be used to improve the accuracy of the model for these compounds in the future.

Nevertheless, Fig. 2 shows that the calculated melting points of ILs based on imidazolium, pyridinium, pyrrolidinium, piperidinium, ammonium, and phosphonium cations with anions, such as $[Tf_2N]$, $[BF_4]$, $[CH_3COO]$, $[MeSO_4]$, $[EtSO_4]$, $[CF_3SO_3]$, $[Br]$, $[CF_3COO]$, $[N(CN)_2]$, $[C(CN)_3]$, $[AlCl_4]$, $[Pf_2N]$, $[PF_6]$, and $[Cl]$ display an acceptable correlation with the literature melting points, if it is considered that the literature data for melting points of ILs usually show a considerable deviation between data reported by different authors. The model is capable of predicting the melting point of all the possible combinations of the types of cations shown in Table 1 with the anions mentioned previously.

7 Conclusions

A group contribution model has been developed to predict the melting points of imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, phosphonium-, and piperidini-

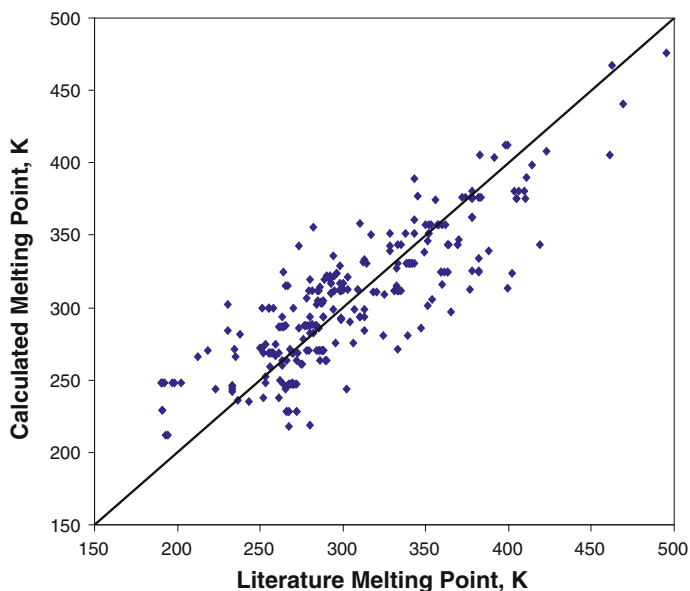


Fig. 2 Plot of literature versus calculated melting points for all 293 data points of 136 studied ILs

um-based ILs with common anions. The proposed model considers the contributions of ionic groups and methylene groups as additive parameters and two simple non-additive characteristic geometric parameters of cations such as symmetry and flexibility.

The average relative deviation of the model is 7.8%, and the average absolute deviation is 22.6 K. 293 Data points for 136 ILs were used in this study. The accuracy of the method developed is within the expected margins, as reported experimental melting-point data have similar deviations. The proposed model can be used for the prediction of melting points of a wide range of ILs, and for the design of these compounds using computer-aided molecular design (CAMD) methods, for their multiple applications. In addition, the model developed for the estimation of the melting points of ILs has advantages over other methods reported in the literature in that it is applicable to a wide range of ILs, and is relatively straightforward, fast, and easy to use.

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References

1. J.H. Davis, *Chem. Lett.* **33**, 1072 (2004)
2. J.F. Brennecke, E.J. Maginn, *AIChE J.* **47**, 2384 (2001)
3. J.D. Holbrey, R.D. Rogers, "Melting Points and Phase Diagrams," in *Ionic Liquids in Synthesis*, ed. by P. Wasserscheid, T. Welton (Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2003)

4. A.R. Katritzky, R. Jain, A. Lomaka, R. Petrukhin, M. Karelson, A.E. Visser, R.D. Rogers, *J. Chem. Inf. Comput. Sci.* **42**, 225 (2002)
5. K.R. Seddon, in *Proceedings of The International George Papatheodorou Symposium, 1999*, ed. by S. Boghosian, V. Dracopoulos, C.G. Kontoyannis, G.A. Voyiatzis, Institute of Chemical Engineering and High Temperature Chemical Processes, Patras
6. A.R. Katritzky, R. Jain, A. Lomaka, R. Petrukhin, U. Maran, M. Karelson, *Cryst. Growth Des.* **1**, 261 (2001)
7. M. Reinhard, A. Drefahl, *Handbook for Estimating Physicochemical Properties of Organic Compounds* (Wiley, New York, 1999)
8. P. Simamora, A.H. Miller, S. Yalkowsky, *J. Chem. Inf. Comput. Sci.* **33**, 437 (1993)
9. L. Constantinou, R. Gani, *AIChE J.* **40**, 1697 (1994)
10. K.G. Joback, R.C. Reid, *Chem. Eng. Commun.* **57**, 233 (1987)
11. J. Marrero, R. Gani, *Fluid Phase Equilib.* **183–184**, 183 (2001)
12. L. Zhao, S.H. Yalkowsky, *Ind. Eng. Chem. Res.* **38**, 3581 (1999)
13. A. Jain, G. Yang, S. Yalkowsky, *Ind. Eng. Chem. Res.* **43**, 7618 (2004)
14. R.L. Gardas, J.A.P. Coutinho, *AIChE J.* **55**, 1274 (2009)
15. R.L. Gardas, J.A.P. Coutinho, *Ind. Eng. Chem. Res.* **47**, 5751 (2008)
16. R.L. Gardas, J.A.P. Coutinho, *Fluid Phase Equilib.* **263**, 26 (2008)
17. I. López-Martín, E. Burello, P.N. Davey, K.R. Seddon, G. Rothenberg, *Chem. Phys. Chem.* **8**, 690 (2007)
18. G.V.S.M. Carrera, L.C. Branco, J. Aires-de-Sousa, C.A.M. Afonso, *Tetrahedron* **64**, 2216 (2008)
19. U. Preiss, S. Bulut, I. Krossing, *J. Phys. Chem. B* **114**, 11133 (2010)
20. Y. Huo, S. Xia, Y. Zhang, P. Ma, *Ind. Eng. Chem. Res.* **48**, 2212 (2009)
21. C. Chiappe, D. Pieraccini, *J. Phys. Org. Chem.* **18**, 275 (2005)
22. R. Abramowitz, S.H. Yalkowsky, *Pharm. Res.* **7**, 942 (1990)
23. A. Jain, G. Yang, S.H. Yalkowsky, *Ind. Eng. Chem. Res.* **43**, 4376 (2004)
24. R.-M. Dannenfelser, S.H. Yalkowsky, *Ind. Eng. Chem. Res.* **35**, 1483 (1996)
25. NIST (2010) IUPAC Ionic Liquids Database (IL Thermo), NIST Standard Reference Database 147, <http://ILThermo.boulder.nist.gov/ILThermo/>. Accessed 25 Jan 2010
26. Merck Chemicals Reagents Catalogue, 2008
27. S. Zhang, X. Lu, Q. Zhou, X. Li, X. Zhang, S. Li, *Ionic Liquids, Physicochemical Properties*, 1st edn. (Elsevier, Amsterdam, 2009), p. 84
28. S. Zhan, N. Sun, X. He, X. Lu, X. Zhang, *J. Phys. Chem. Ref. Data* **35**, 1475 (2006)
29. CYTEC, Product Data Sheet, Phosphine & Phosphorus Specialities (2008)
30. H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal. A* **182–183**, 419 (2002)
31. G. Law, P. Watson, *Langmuir* **17**, 6138 (2001)