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RESEARCH ARTICLE

A Group Contribution Method for Predicting the Freezing Point of Ionic Liquids

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Abstract
A simple group contribution method for the prediction of the freezing point for several ionic liquids is presented. Liquids have a characteristic temperature, known as their freezing point, at which they turn into solids. The melting point of a solid should theoretically be the same as the freezing point for the liquid. Greater differences between these quantities can be observed in ionic liquids. Some ionic liquids display substantial supercooling while being cooled at relatively high temperature. Experimental data from the freezing point (not melting point) for 40 ionic liquids were used to obtain the contributions for the cation-anion groups in a correlation set. The optimum parameters of the method were obtained using a genetic algorithm-based on multivariate linear regression. Then, the freezing points for another 23 ionic liquids were predicted, and the results were compared with experimental data available in the literature. The results show an average deviation of 5 %.

Keywords
ionic liquids, freezing point, group contribution method, property estimation, genetic algorithms

1 Introduction

Ionic liquids (ILs) are a new generation of solvents for catalysis and synthesis, which has been proven as the new possible successful replacements for conventional media in new technologies [1]. ILs have been the object of increasing attention due to their unique physicochemical properties, such as high thermal stability, large liquidus range, high ionic strength, high solvating capacity, negligible vapour pressure, and nonflammability, which make them the most suitable solvents for green chemistry and clean synthesis [2-4].

It is well known that the characteristic properties of ionic liquids can vary with the choice of anion and cation. The structure of an ionic liquid directly impacts on its properties, particularly the phase transition temperatures [5]. The thermal behaviour of many ionic liquids is relatively complex [6]. Melting happens when molecules or ions fall out of their crystal structures and turn into a disordered liquid. The glass transition goes from solid to amorphous solid; but even crystalline solids may have some amorphous portion resulting in the same IL sample is likely having both a glass-transition temperature and a melting temperature. The freezing point (T_f) has the same meaning as the melting point while an opposite process [5]. In general, glass transition temperatures, melting points and freezing points are highly desirable [7-9]. The freezing point theoretically occurs at the same temperature as the melting point. However, both temperatures could be different for ionic liquids. Some ILs display substantial supercooling while being cooled from relatively high temperature [5]. Note that the supercooling phenomenon refers to a non-equilibrium situation, while freezing point is an equilibrium property. The ILs presenting a freezing transition upon cooling show a strong tendency for forming crystals. Then, these ILs should be subjected to a faster cooling rate to avoid crystallization during a freezing transition [10]. Figure 1 shows a comparison between melting point values and freezing point values for ionic liquids formed by 1-ethyl-3-methyl imidazolium ([emim]$^+$) cation and different anions. This Figure shows the great difference between melting temperature and freezing temperature value for ILs.

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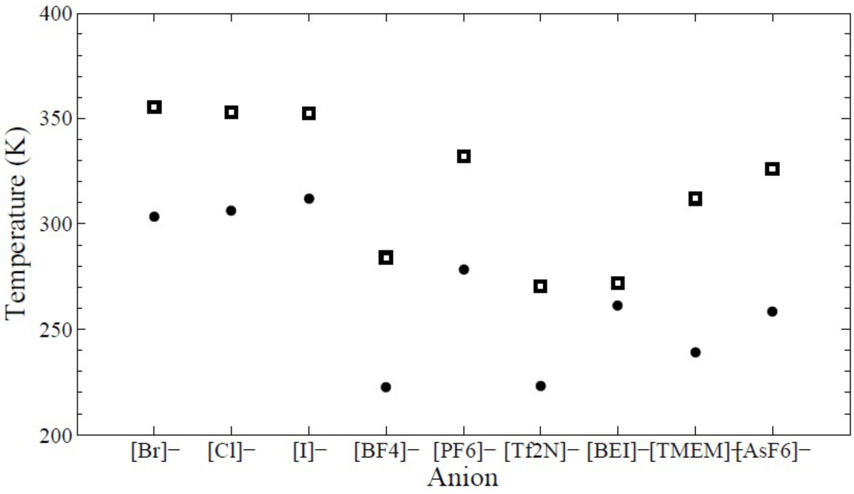


Fig. 1 Comparison between values of melting point (□) [5], and freezing point (●) [3] of [emim]$^+$[X]$^-$. In this figure: bromide [Br]$^-$, chloride [Cl]$^-$, iodide [I]$^-$, tetrafluoroborate [BF$_4$]$^-$, hexafluorophosphate [PF$_6$]$^-$, bis(trifluoromethylsulfonyl)imide [Tf2N]$^-$, bis(pentafluoro-ethylsulfonyl)imide [BEI]$^-$, tris(trifluoromethylsulfonyl)methyide [TMEM]$^-$, and hexafluoroarsenic [AsF$_6$]$^-$.

The T_f is difficult to be determined experimentally because transition could take place over a wide temperature range, and it is depend on conditions such as measuring method, experiment duration, and pressure [11]. The increasing utilization of ILs in chemical and industrial processes requires reliable thermophysical properties for a better understanding of ILs' thermodynamic behaviour and for the development of thermodynamic models [12].

ILs typically consist of a large organic cation and an inorganic anion. There are not any limitations for the number of possible ILs since there is a large number of cations and anions that can be combined [13]. It has been estimated that up to 10^6 different ionic liquids may exist [14], and that for this vast number of substances is essential to increase their understanding in order to allow accurate predictions of their properties. It was shown that extending estimation procedures originally derived from organic substances as the group contribution methods (GCMs), instead of developing complete new procedures for treating these new fluids, is a reasonable way for obtaining such hypothetical properties needed for other calculations [7-9] for ILs. However, no applications for the estimation of the freezing point (not melting point) has been published yet.

In this work, freezing points (not melting points) for several ILs were correlated and predicted using an accurate GCM with structural groups for the cation-anion parts.

2 Method

2.1 Computational calculations

The mathematical foundation for the GCM is based on the principle of polylinearity [15]. Multiple linear or non-linear regressions commonly used in GCM studies [16]. Multiple linear or non-linear regressions fit a set of data points (xi, y) into a function y that is a linear combination for any number of functions for the independent variables xi [12].

$$y(x) = a_1 + a_2 x_1 + a_3 x_2 + \ldots + a_m x_{m-1} \tag{1}$$

Thus, the following equation was used for calculation of the freezing point T_f:

$$T_f = C + \sum_i n_i \Delta t_i \tag{2}$$

where T_f represents the property value, C is a regression constant, n_i is the number of occurrences for each molecular group, and Δt_i is the contribution value for each group obtained by the regression analysis.

In the ILs' case, several authors show that a better approach can be obtained by separately using contributions for the cation and anion [17]. Then, T_f for ILs can be expressed as:

$$T_f = C + \sum_i n_i \Delta t_{c_i} + \sum_i n_j \Delta t_{a_j} \tag{3}$$

where n_i and n_j are the occurrence for the groups i and j in the compound, Δt_c is the contribution of the cation group, and Δt_a is the anion group contribution for the freezing point.

The regression method was optimized by genetic algorithms (GA) [18] so as to minimize the difference between calculated and experimental T_f. The regression method was based on the minimization of an objective function (*OF*) as follow:

$$OF = \sum_{i=1}^{N} \left[T_f^{calc} - T_f^{lit} \right]_i^2 \tag{4}$$

where the minimized merit function is the sum of the distances between the regression values and the experimental data points.

The full methodology was programmed in MATLAB [19]. Table 1 shows the selected parameters for the GA optimization.

2.2 Database

In this GCM, experimental data from 63 ILs with the freezing point temperatures in a range from 185 K to 466 K were used. Database was taken from [5, 20].

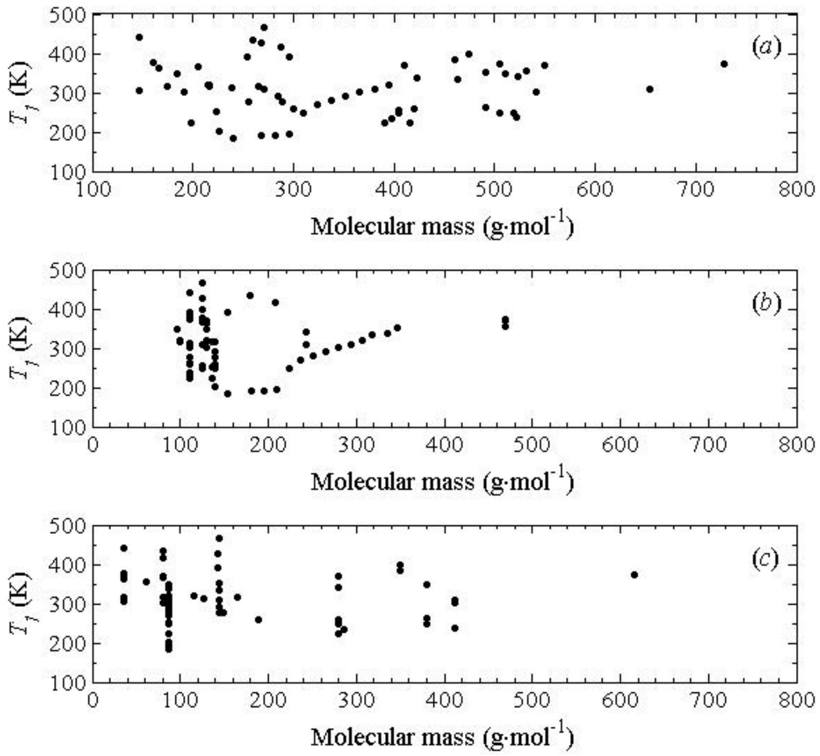


Fig. 2 Freezing point temperatures as a function of the molecular mass for all ionic liquids used in this study. (a) Total mass distribution, (b) cation distribution, and (c) anion distribution.

Table 1 Parameters used in the genetic algorithm.

GA parameter	Value
Number of generations (*Gen*)	500
Number of individuals (N_i)	200
Length of chromosome (*L*)	20
Length of an individuals (L_i)	80
Crossover probability (*Cros*)	0.8
Mutation probability (*Mut*)	0.1
Crossover operador	Multipoint
Mutation operador	Binary
Objective function	Eq. (4)

Figure 2 shows a general picture of the considered ranges for T_f and ILs. These values are of especial importance for verifying acceptable range of coverage for T_f in this study. Data were selected from specific databases and correspond to those claimed as experimentally determined with uncertainties below than ±1 K. Data available in the literature obtained from theoretical methods, correlations or extrapolations of any kind were not considered. Data which accuracy were determined by the authors as not able to be guaranteed for any reason (presence of impurities, fluid instability, or equipment problems) were not considered [21].

3 Results and discussion

Functional group contributions were calculated using experimental data from 40 ILs, and these values were used for estimating T_f for a wide range of ILs. The value associated with the structural group was defined as 0 (zero), when the group does not appear in the substance and n, when the group appears n-times in the substance. Functional groups were divided into groups for the cation part and for the anion part, and the final equation for this model was:

$$T_f\left(\mathrm{K}\right) = 98.599 + \sum_{i=1}^{10} n_i \Delta t_{c_i} + \sum_{j=1}^{21} n_j \Delta t_{a_j} \tag{5}$$

where n_i and n_j are the occurrence of the groups i and j in the IL, Δt_c is the cation group contribution, and Δt_a is the anion group contribution for T_f, and $C = 98.599$ is a regression constant.

Cation groups included imidazolium, pyridinium, pyrrolidinium, phosphonium, and ammonium. The contribution values determined for the 10 cation groups are presented in Table 2. Anion groups included halides, pseudohalides, sulfonates, tosylates, imides, borates, phosphates, carboxylates, and metal complexes. Table 3 shows the contribution values determined for the 21 anion groups.

Once the correlation was done and optimum values for the groups were calculated, other 23 ILs that were not used for this calculation were used for model testing. For this validation set, the reported data of T_f can vary from 224 K to 399 K.

Table 2 Cation groups considered in the GCM.

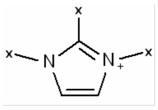
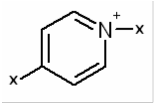
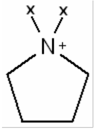
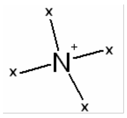
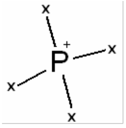
No.	Name	Group	Δt_c	Std. Dev.	No. Occurrence
1	Imidazolium		39.698	0.698	30
2	Pyridinium		82.227	1.445	4
3	Pyrrolidinium		12.868	0.226	2
4	Ammonium		13.890	0.244	2
5	Phosphonium		–48.738	0.857	2
6	Substituted (–X)	–H	38.623	0.679	22
7		$–CH_3$	68.819	1.210	40
8		$–CH_2–$	1.344	0.024	35
9		–CH<	– 79.375	1.395	2
10		–N<	21.626	0.380	2

Table 3 Anion groups used in the GCM.

No.	Group	Δt_a	Std. Dev.	No. Occurrence
1	=CH–	21.765	0.383	2
2	>C<	9.910	0.174	2
3	–COO	13.484	0.237	2
4	–HCOO	13.531	0.238	2
5	–O– [–O]	–9.850	0.173	2
6	–N– [>N–]	–5.493	0.097	5
7	$–NO_3$	–4.482	0.079	2
8	$–SO_2–$	8.757	0.154	8
9	$–CF_3$	–41.448	0.729	9
10	$–CF_2–$	–1.811	0.032	3
11	–F	–4.930	0.087	17
12	–Cl	10.923	0.192	4
13	–Br	10.213	0.180	5
14	–P [>P<]	33.726	0.593	6
15	–B [>B<]	–20.084	0.353	10
16	–I	–3.753	0.066	2
17	>As<	–28.174	0.495	2
18	$–CB_{11}H_6$	–5.603	0.098	2
19	$–CB_{11}H_{12}$	66.553	1.170	2
20	=CH– (ring)	8.067	0.142	2
21	=C< (ring)	3.132	0.055	2

Correlation and validation sets were selected randomly, considering that molecules are decomposed into fragments and that all fragments with adequate frequency are in the correlation set for the group contribution methods [12].

Finally, after the model was defined, values of T_f were calculated for all used ILs. Model accuracy was checked via T_f calculated values and experimental data from the literature by using the average relative absolute deviation for each IL ($|\%\Delta T_f|$) and for the total set (AARD). Deviations were calculated as follows:

$$\left|\%\Delta T_f\right| = \left|\frac{T_f^{calc} - T_f^{lit}}{T_f^{lit}}\right| \cdot 100 \tag{6}$$

$$\text{AARD} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{T_f^{calc} - T_f^{lit}}{T_f^{lit}}\right|_i \tag{7}$$

Table 4 summarizes deviations for all ILs using the proposed GCM. Results show that the GCM can estimate T_f for several ILs with enough accuracy: an AARD lower than 5.34 % for the 40 ILs used in the correlation set and an AARD lower than 5.25 % for the other 23 ILs used on the prediction step.

Figure 3 shows an overview of T_f prediction accuracy for the correlated set with 40 ILs and for the predicted set with 23 ILs, with a correlation coefficient R^2 of 0.9472 and 0.9138, respectively. Note that for the total set (63 ILs) the R^2 is 0.9397.

Table 4 Summary of deviations in the estimation of the freezing point temperature of ILs.

Deviations	Correlation Set	Prediction Set	Total Set
No. ILs	40	23	63
AARD	5.34	5.25	5.30
$\%\Delta T_{f\,min}$	0.00	0.15	0.00
$\%\Delta T_{f\,max}$	19.37	15.46	19.37
$\lvert\%\Delta T_f\rvert < 10$	34	17	51
$\lvert\%\Delta T_f\rvert > 15$	2	1	3
R^2	0.9472	0.9138	0.9397

Table 5 shows a comparison between the literature values and the calculated values for T_f obtained from the GCM proposed in this work. Table 6 illustrates the application of the proposed GCM for some ILs. In general, the low deviations found using the proposed method (AARD of 5 %, AARD_{max} a slightly higher than 20 %) represent a great increase in accuracy for the prediction of this important accuracy property.

In recent studies, this author has found that thermal properties strongly depend on the IL structure [7-9]. The result obtained from this study shows that T_f for ILs depends on the type of cation. Table 7 shows ranges of T_f for some ILs based on different cation, and the correlation coefficients obtained for the different cation types. Remarkable differences in T_f are also observed when changing the anions, while a simple extension of alkyl chain greatly affects imidazolium cation T_f. Table 8 shows the recommended T_f ranges of for the most common imidazolium-based ILs, and the correlation coefficient based on different cation types.

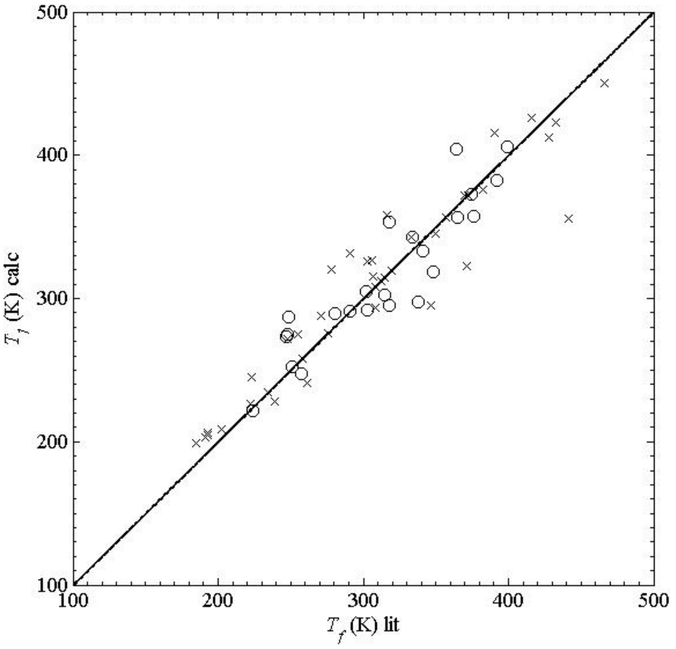


Fig. 3 Comparison between literature and calculated values of the freezing point temperatures of ILs using the proposed GCM for: correlated set (×) with $R^2 = 0.9472$, and predicted set (○) with $R^2 = 0.9138$.

4 Conclusions

This study presents a simple group contribution method for the prediction of the freezing point temperature for several ionic liquids.

Based on the results and discussions presented in this study, the following conclusions are obtained:

The proposed method allows the freezing point estimation of several IL classes composed of 10 cation groups and 21 anion groups in a wide range of temperatures (185 to 466 K). For a database consisting of 63 ILs, the AARD observed was 5.3 %. The great differences in the chemical structure and the physical properties of the ionic liquids considered in the study cause additional difficulties to the problem the proposed group contribution method has been able to handle.

The group contribution method can estimate the freezing point decomposition temperature for several ionic liquids with low deviations. Method consistency has been checked by using experimental values for freezing points and by comparing them with values calculated by the proposed method.

The calculated values with the proposed method are considered as accurate enough for engineering calculations and for generalized correlations, among other uses.

Table 5 Calculated freezing point temperatures using the proposed GCM.

Cation	Anion	T_f^{lit} (K)	Ref.	T_f^{calc} (K)	$\lvert\%\Delta T_f\rvert$
	Correlated set				
1,2-Dimethyl-3-ethylimidazolium	Bis[(trifluoromethyl)sulfonyl]imide	255.15	[20]	275.22	7.87
1,2-Dimethyl-3-ethylimidazolium	Bis(pentafluoroethylsulfonyl)imide	248.15	[20]	271.60	9.45
1,2-Dimethyl-3-ethylimidazolium	Hexafluorophosphate	466.15	[5]	450.25	3.41
1,3-Dimethylimidazolium	Tetrafluoroborate	346.75	[20]	294.76	14.99
1-Butyl-2,3-dimethylimidazolium	1-Carbon icosahedral	390.15	[20]	415.34	6.46
1-Butyl-3-methylimidazolium	Tetrafluoroborate	202.15	[20]	208.79	3.28
1-Butyl-3-methylimidazolium	Trifluoromethanesulfonate	276.05	[5]	276.05	0.00
1-Butyl-4-(dimethylamino)pyridinium	Bromide	433.00	[20]	423.16	2.27
1-Ethyl-2,3-dimethylimidazolium	1-Carbon icosahedral	428.15	[20]	412.65	3.62
1-Ethyl-3-methylimidazolium	Bis[(trifluoromethyl)sulfonyl]imide	223.15	[20]	245.03	9.80
1-Ethyl-3-methylimidazolium	Tetrafluoroborate	222.65	[20]	226.10	1.55
1-Ethyl-3-methylimidazolium	Bromide	303.15	[20]	326.12	7.58
1-Ethyl-3-methylimidazolium	Chloride	306.15	[20]	326.83	6.75
1-Ethyl-3-methylimidazolium	Nonafluoro(n-butyl)trifluoroboratenonafluoro	234.15	[20]	234.15	0.00
1-Ethyl-3-methylimidazolium	Bis(pentafluoroethylsulfonyl)imide	261.15	[20]	241.41	7.56
1-Ethyl-3-methylimidazolium	Iodide	312.15	[20]	312.15	0.00
1-Ethyl-3-methylimidazolium	Hexafluoroarsenic	258.15	[20]	258.15	0.00
1-Ethyl-3-methylimidazolium	Hexafluorophosphate	278.15	[5]	320.05	15.06
1-Ethyl-3-methylimidazolium	Hexachloride-1-carbon icosahedral	382.15	[5]	375.84	1.65
1-Ethyl-3-methylimidazolium	Tri(trifluoromethylsulfonyl)methyide	239.15	[5]	227.74	4.77
1-Ethyl-3-methylimidazolium	Hexabromide-1-carbon icosahedral	372.15	[5]	371.58	0.15
1-Heptyl-3-methylimidazolium	Tetrafluoroborate	191.25	[20]	202.64	5.96
1-Hexadecyl-4-methylpyridinium	Hexafluorophosphate	333.15	[20]	342.77	2.89
1-Hexyl-4-(dimethylamino)pyridinium	Bromide	416.00	[20]	425.84	2.37
1-Isopropyl-3-methylimidazolium	Hexafluorophosphate	308.15	[5]	308.15	0.00
1-Nonyl-3-methylimidazolium	Tetrafluoroborate	193.15	[20]	206.30	6.81
1-Octadecyl-4-methylpyridinium	Hexafluorophosphate	350.15	[5]	345.46	1.34
1-Octyl-3-methylimidazolium	Tetrafluoroborate	192.65	[20]	204.47	6.13
1-Pentadecyl-3-methylimidazolium	Tetrafluoroborate	308.15	[5]	293.57	4.73
1-Pentyl-3-methylimidazolium	Tetrafluoroborate	185.15	[20]	198.98	7.47
1-Propyl-2,3-dimethylimidazolium	Chloride	316.00	[20]	358.37	13.41
1-Propyl-2,3-dimethylimidazolium	Hexafluorophosphate	291.15	[5]	331.59	13.89
1-Undecyl-3-methylimidazolium	Tetrafluoroborate	270.65	[20]	288.20	6.48
2,4,5-Trimethylimidazolium	Chloride	441.15	[20]	355.68	19.37
N,N-Dimethylpyrrolidinium	Hydrogen maleate	319.65	[20]	319.65	0.00
N,N-Dimethylpyrrolidinium	Hydrogen phthalate	314.65	[20]	314.65	0.00
Tetrabutylammonium	Tri(trifluoromethylsulfonyl)methide	307.15	[5]	315.73	2.79
Tetraethylammonium	Bis[(trifluoromethyl)sulfonyl]imide	371.15	[20]	322.27	13.17
Tridecylmethylphosphonium	Bromide	369.85	[20]	371.64	0.49
Tridecylmethylphosphonium	Nitrate	356.95	[20]	356.95	0.00

Predicted set					
1,2-Dimethyl-3-ethylimidazolium	Bromide	365.15	[20]	356.31	2.42
1,2-Dimethyl-3-ethylimidazolium	Chloride	376.15	[20]	357.02	5.09
1-Butyl-3-methylimidazolium	Bis[(trifluoromethyl)sulfonyl]imide	257.15	[20]	247.72	3.67
1-Decyl-3-methylimidazolium	Tetrafluoroborate	248.45	[20]	286.85	15.46
1-Dodecyl-3-methylimidazolium	Tetrafluoroborate	280.55	[20]	289.54	3.21
1-Ethyl-2,3-dimethylimidazolium	Bis[(trifluoromethyl)sulfonyl]imide	248.15	[20]	275.22	10.91
1-Ethyl-2,3-dimethylimidazolium	Hexachloride-1-carbon icosahedral	399.15	[20]	406.03	1.72
1-Ethyl-3-methylimidazolium	1-Carbon icosahedral	392.15	[5]	382.46	2.47
1-Hexadecyl-3-methylimidazolium	Tetrafluoroborate	318.25	[5]	294.92	7.33
1-Hexadecyl-3-methylpyridinium	Hexafluorophosphate	334.15	[20]	342.77	2.58
1-Octadecyl-3-methylimidazolium	Hexafluorophosphate	337.65	[5]	297.61	11.86
1-Propyl-2,3-dimethylimidazolium	Bis(pentafluoroethylsulfonyl)imide	247.15	[20]	272.95	10.44
1-Tetradecyl-3-methylimidazolium	Tetrafluoroborate	302.45	[5]	292.23	3.38
1-Tridecyl-3-methylimidazolium	Tetrafluoroborate	290.45	[5]	290.89	0.15
N-Butylpyridinium	Bis[(trifluoromethyl)sulfonyl]imide	224.00	[20]	221.42	1.15
N-Butylpyridinium	Tetrafluoroborate	251.00	[20]	252.50	0.60
N-Butylpyridinium	Bromide	315.00	[20]	302.51	3.96
Tetrabutylammonium	Bis[(trifluoromethyl)sulfonyl]imide	341.15	[20]	333.02	2.38
Tetraethylammonium	Bis(pentafluoroethylsulfonyl)imide	348.15	[20]	318.65	8.47
Tetraethylammonium	Tetrafluoroborate	318.15	[20]	353.34	11.06
Tetraethylammonium	Chloride	364.15	[20]	404.07	10.96
Tetraethylammonium	Tri(trifluoromethylsulfonyl)methyide	302.15	[5]	304.98	0.94
Tridecylmethylphosphonium	Chloride	374.15	[20]	372.36	0.48

Table 6 Examples of application of the GCM in the prediction of the T_f for some ILs.

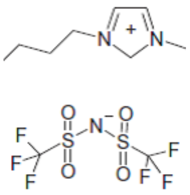
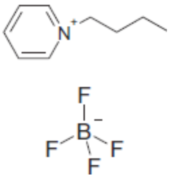
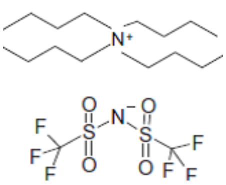
Structure	Group	Contribution	Occurrence	$\sum n_i \Delta t_i$	T_f^{calc} (K)	T_f^{lit} (K)	$\lvert\%\Delta T_f\rvert$
IL: 1-Butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide							
	Imidazolium	39.698	1	219.991	247.72	257.15 [20]	3.67
	–H	38.623	1				
	$–CH_2–$	1.344	3				
	$–CH_3$	68.819	2				
	–N–	–5.493	1	–70.875			
	$–SO_2–$	8.757	2				
	$–CF_3$	–41.448	2				
IL: N-Butylpyridinium tetrafluoroborate							
	Pyridinium	82.227	1	155.078	252.50	251.00 [20]	0.60
	$–CH_2–$	1.344	3				
	$–CH_3$	68.819	1				
	>B<	–20.084	1	–39.804			
	–F	–4.930	4				
IL: Tetrabutylammonium bis[(trifluoromethyl)sulfonyl]imide							
	Ammonium	13.890	1	305.29	333.02	341.15 [20]	2.38
	$–CH_2–$	1.344	12				
	$–CH_3$	68.819	4				
	–N–	–5.493	1	–70.875			
	$–SO_2–$	8.757	2				
	$–CF_3$	–41.448	2				

Table 7 Ranges and correlation coefficients of T_f for some ionic liquids.

Ionic Liquids	T_f range (K)	N	R^2
1-*alkyl*-3-methylimidazolium	180–400	30	0.9381
N-*alkyl*-*N,N*-dimethylimidazolium	240–470	13	0.9148
Tetra-*alkyl*-ammonium	300–380	7	0.8945
N-*alkyl*-pyridinium	220–320	3	0.9954
N-methyl-*N*-*alkyl*-pyridinium	330–350	5	0.9821
N-methyl-*N*-*alkyl*-pyrrolidinium	310–320	2	1.0000
Tetra-*alkyl*-phosphonium	350–380	3	0.9797

Table 8 Ranges and correlation coefficients of T_f for some imidazoium-based ionic liquids.

Anion	Cations	T_f range (K)	N	R^2
[Cl]	[$C_n$mim], [$C_{n,n}$im]	300–380	4	0.8513
[Br]	[$C_n$mim], [$C_{n,n}$im]	530–590	3	0.9627
[BF_4]	[$C_n$mim], [$C_{n,n}$im]	180–350	15	0.9325
[PF_6]	[$C_n$mim], [$C_{n,n}$im], [*i*-C_3mim]	370–470	4	0.9680
[Tf_2N]	[$C_n$mim], [$C_{n,n}$im]	220–260	4	0.9082
[BEI]	[$C_n$mim], [$C_{n,n}$im]	240–270	3	0.9997

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