

## A Semi-Classical Group-Interaction Contribution Method for the Prediction of the Melting Temperature of Ionic Liquids

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### Abstract

The melting temperature ( $T_m$ ) of ionic liquids (ILs) was estimated with a group-interaction contribution method. This temperature is very important for modeling solid-liquid equilibrium and selecting ionic liquids as reaction media, among other things. The proposed method, based on the group-interaction contribution approach, uses two-order contributions and a correction

term. A comprehensive database of 684 ionic liquids with different molecular structures was used to obtain all interaction contribution parameters and correction terms for all groups in the ionic liquids, including a wide range of cation and anion groups. The results showed that with an average absolute relative deviation of 5.04% and a correlation coefficient of 0.85, this linear model represents a reliable and simple approach for the estimation of the melting temperature of diverse ionic liquids based on knowledge of their molecular structure. Taking into account isomerism, it represents an advantage over traditional group contribution methods.

**Keywords:** Group-Interaction contribution, Ionic liquids, Melting temperature, Molecular structure, Property estimation.

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## 1. Introduction

The development of less-polluting solvents and safe processes is nowadays a high priority on the agenda for "green chemistry". There is a pressing need to rethink the design of unsafe chemical processes so that younger generations inherit a healthy and safer environment. In recent years, ionic liquids, salts that are liquids at low temperatures [1], have received the most attention as alternatives to volatile organic solvents in numerous fields. These include reactive chemistry, mineral processing, and separation processes. The fact that ionic liquids are generally viewed as safe and environmentally friendly is attributed to their negligible vapor pressure and wide liquid range [2].

However, the widespread industrial use of ILs is tributary to the knowledge of their thermal, physical, chemical, thermodynamic, and transport properties. The present study is focused on the estimation of the melting point of a variety of ionic liquids by means of the group interaction contribution (GIC) method. Melting occurs when the molecules or ions comprising a solid fall out of their crystal structures to become disordered liquids [3]. In relation to ionic liquids, the melting temperature is important in determining the liquid use range (thus, the use of ILs as reaction media) as well as modeling the solid-liquid equilibrium of systems involving this class of compounds.

Different approaches have been proposed in the literature for predicting the melting point of ionic liquids. Group Contribution (GC) and Quantitative Structure-Property Relationship (QSPR) emerged as the most commonly used methods for ILs' melting point estimation. Other methods include Artificial Neural Network, COSMO-RS, Chemical homology, and machine learning. More details on various approaches for the prediction of the melting point of ionic liquids can be found in the review paper by Valderrama [4]. This author further discusses fundamental issues related to this property and provides an in-depth analysis of the different

predictive tools that have been proposed by various researchers. The reported correlation coefficient ( $R^2$ ) ranged between 0.54 and 0.93, while the average absolute relative deviation (AARD) was between 2.5 and 29.3%.

In this study, a comprehensive data set has been used to develop a predictive model for ionic liquids based on Group–interaction contributions (GIC). To the best of our knowledge, this is the first account of the use of GIC for predicting the melting point of ionic liquids. It is worth noting that Group–interaction contribution (GIC) methods were derived to address the major limitation of conventional group contribution methods [5], i.e., the inability to distinguish between isomers. Thus, the quest for more accurate predictions motivated this study, in which an approach similar to that proposed by Marrero and Pardillo [6] is used. Altogether, 684 ILs based on various cations and anions have been used to develop the proposed GIC model.

## 2. Methodology

### 2.1 Data Set

In order to develop the GIC-based model presented in this study, a large database was considered. Large databases are advisable as they ensure a wide applicability range for the developed correlations. Altogether, the database comprised 684 ionic liquids, ranging from 180.65 to 495,050 K. These melting points were obtained from the work published by Zhang and co-researchers [7] and [8]. For obvious reasons, some ionic liquids have two or more different melting temperatures reported by different groups. Bearing in mind the non-existence of a recommended standard procedure for melting point measurements, no ground could be found to select the more reliable data points. Hence, all reported data for melting points were considered. This explains why the number of data points is larger than that of ionic liquids.

Tables 1 and 2 show all the anions and cations involved in the investigated ionic liquids. There were altogether 18 cation and 44 anion types represented. It emerges that experimental studies related to  $T_m$  measurements mostly covered imidazolium, ammonium, phosphonium, piperidinium, and pyrrolidinium-based ionic liquids. This could be expected as the most commercially available ionic liquids comprise these cations.

**Table 1: Cations encountered in the studied ionic liquids: the percentage indicates the number of the given cation out of the total number of ILs comprising the data base.**

Class of ILs	Abbreviation	No of ILs
Imidazolium	IM	230

Benzotriazolium	Bt	12
Triazolium	Taz	49
Pyridinium	py	41
Sulfonium	S	10
Ammonium	N	201
Piperidinium	PP	09
Pyrrolidinium	Pn <sub>1</sub> n <sub>2</sub>	38
Piperazinium	Pip n <sub>1</sub> n <sub>2</sub>	01
Caprolactam	NHC	03
Butyrolactam	PY or Az	01
Morpholinium	MO	19
Tetrazolium	Tetaz	07
Oxazolidinium	OX	06
Amino acids	AA	23
Guanidinium	Guan	12
Phosphonium	P	19
Pyrimidine	(R <sub>1</sub> R <sub>2</sub> )N=(R <sub>3</sub> R <sub>4</sub> )	03

Table 2: *Anions* encountered in the studied ionic liquids: the percentage indicates the number of ILs containing the given cation out of the total number of ILs comprising the data base.

Class of ILs	Abbreviation	No of ILs
Hexafluorophosphate	PF <sub>6</sub>	66

Tetrafluoroborate	$\text{BF}_4$	69
Bis((trifluoromethyl)sulfonyl)imide	TFSI or $\text{NTf}_2$	109
Halide	X	92
Alkylsulfate	$\text{R}_1\text{SO}_4$	19
Carboxylates	$\text{R}_1\text{COO}$	25
Di(hydrogen or alkyl)phosphate	$\text{R}_2\text{PO}_4$	03
Trifluoromethylsulfonate	TfO	26
Trifluoroacetate	TfA or TA	04
Dicyanamide	dca	09
Tris (trifluoromethylsulfonyl) methide	$\text{Tf}_3\text{C}$ or Me	04
5-nitrotetrazolate	Ntet	02
4,5-dinitroimidazolate	Nlmi	04
Azide	$\text{N}_3$	02
Perchlorate	$\text{ClO}_4$	24
Nitrite	$\text{NO}_2$	01
Nitrate	$\text{NO}_3$	50
Sulfonate	$\text{R}_1\text{SO}_3$	30
Borate	$\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{B}$	63
Dinitramide	$\text{N}(\text{NO}_2)_2$	02
Tetrachloroaluminate	$\text{AlCl}_4$	02
Hexafluoroarsenate	$\text{AsF}_6$	01
Hexafluoroantimonate	$\text{SbF}_6$	01
Hexafluoroniobate	$\text{NbF}_6$	01

Oxypentafluorotungstate	WOF <sub>5</sub>	01
Thiocyanate	SCN	06
bicarbonate	HCO <sub>3</sub>	01
4,4,4-trifluoro-1-(2-thenoyl)-1,3-butanedionate	(CF <sub>3</sub> CO)CH (COthiophe ne)	08
4,4,4-trifluoro-1-(2-furyl)-1,3-butanedionate	(CF <sub>3</sub> CO)- CH- (COfuran)	05
2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate	(Me <sub>2</sub> CCO)C H(CO(CF <sub>2</sub> ) <sub>2</sub> CF <sub>3</sub> )	05
1,1,1,5,5,5-hexafluoro-2,4-pentanedionate	(CF <sub>3</sub> CO) <sub>2</sub> C H	14
bis(nonafluorobutane-1-sulfonyl)imide	NNF <sub>2</sub>	02
Saccharinate	Sac	04
N-(trifluoromethylsulfonyl) pentafluoroethylsulfonamide	C1C2	05
bis(methylsulfonyl)imide	MSI	05
2,2,2-trifluoro-N-(trifluoromethylsulfonyl) acetamide	TSAC	11
bis((perfluoroethane) sulfonyl)imide	BETI	06
bis(fluorosulfonyl) imide	FSI	02

## 2.2. Proposed model

In the present study, molecular structure was related to the melting point of ionic liquids through a three-level estimation: first-order contribution and second-order contribution. This was done according to principles outlined in previous works owed to Marrero and Pardillo [5] and Mokadem et al. [9]. The method suggested by these researchers is articulated around these three points.

As shown in the literature, a property denoted  $T_m$  can be modeled via GIC by means of the following correlations:

$$T_m(K) = A + \sum_j n_j \Delta C_j + \sum_k m_k \Delta D_k + \sum_i f_i \Delta C_i \quad (1)$$

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  $\Delta C_j$  are the group-interaction contributions for the first and  $\Delta D_k, \Delta C_i$  second-order group respectively, and  $A$  and  $f_i$  are adjustable model parameters.

The step procedure shown in Figure 2 was used to determine the adjustable parameters and group-interaction values for the model.

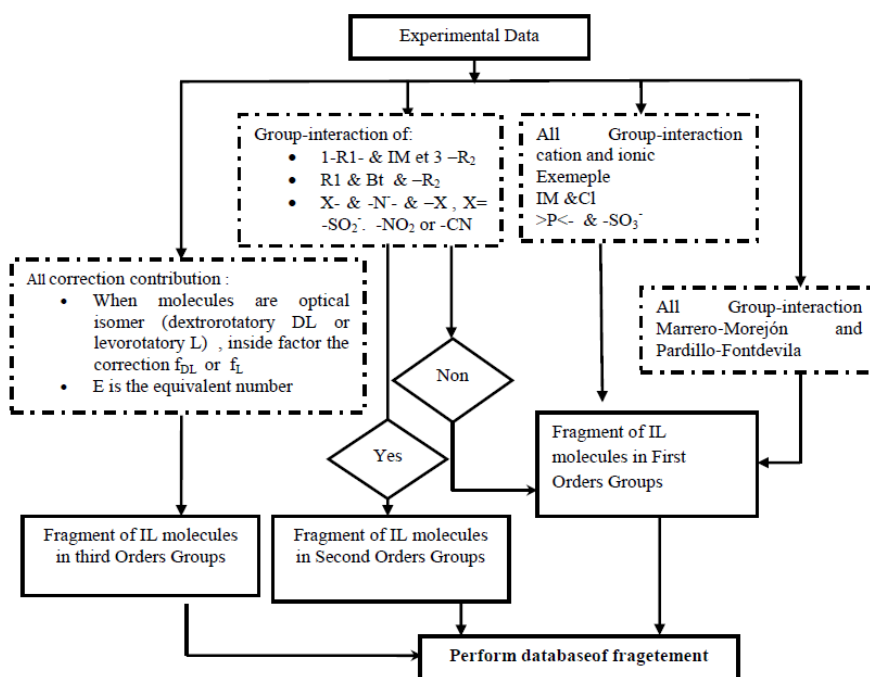


Figure 2: Computational algorithm for the GIC model

The objective function, the average absolute deviation (AAD), the percent average relative deviation (%AARD) and the correlation coefficient ( $R^2$ ) were calculated as a means to assess the performance of the developed model, according to the following equation:

$$F = \sum_{i=1}^n (T_{m_i}^{Exp} - T_{m_i}^{cal})^2 \quad (2)$$

$$AAD = \frac{100}{n} \sum_{i=1}^n |T_{m_i}^{exp} - T_{m_i}^{cal}| \quad (3)$$

$$\%AARD = \frac{100}{n} \sum_{i=1}^n \left| \frac{T_{m_i}^{cal}}{T_{m_i}^{exp}} - 1 \right| \quad (4)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n \left| \frac{T_{m_i}^{cal}}{(T_{m_i}^{ext} - T_{m_i}^{exp})} \right|^2}{\sum_{i=1}^n \left| \frac{T_{m_i}^{cal}}{(T_{m_i}^{exp} - \text{average}(T_{m_i}^{exp}))} \right|^2} \quad (5)$$

As part of this study, the validation set comprised 505 data points used to test the developed model. Although the correlation and validation sets were selected randomly, care was taken to ensure that during the modeling process, molecules were decomposed into fragments, with all the groups found to have adequate frequency in the selected ILs.

### 3. Results and discussion

In order to estimate the melting temperature of ILs, the contributions of the group interaction were calculated from the experimental data of different ionic liquids according to the procedure presented in Figure 5. The final equation for this model, obtained through linear regression, was as follows:

$$T_m(K) = 292.160 + \sum_j n_j \Delta C_j + \sum_k m_k \Delta D_k + f_E \times E + f_L + f_{DL} \quad (6)$$

However, in the case of optical isomers (dextrorotatory DL or levorotatory L), the corresponding correction factors were optimized as  $f_L = -127.516$  K and  $f_{DL} = 0$  K to be used in this equation:

$$T_m(K) = 292.160 + \sum_j n_j \Delta C_j + \sum_k m_k \Delta D_k - 69.91 \times E - 127.51 \times f_L \quad (7)$$

First - and second-order group-interaction contribution parameters are reported in Tables 3 and 4, respectively. First-order group interactions were determined for all sub-structures comprising the examined ionic liquids and cations. Second-order group interaction contribution values were obtained for all functional groups and anions available in the

ionic liquids' database. Altogether, 268 first-order and 16 second-order interaction parameters were obtained.



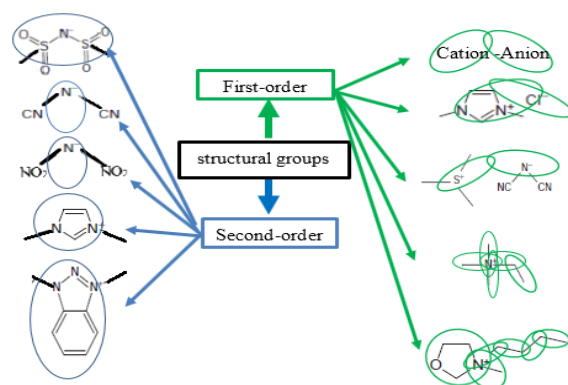


Figure 1: Description of the interaction between groups for the GIC model

Table 3: First-order structural groups and their interactions and contributions

No	Interactions	$\Delta C_i / K$	No	Interactions	$\Delta C_i / K$
01	-CH <sub>3</sub> &-CH <sub>2</sub> -	0.373	13	IM & NbF <sub>6</sub>	38.630
02	-CH <sub>3</sub> &>CH-	26.566	6	Bt & -CH <sub>3</sub>	0.000
03	-CH <sub>3</sub> &>C<	-3.812	13	Bt &- CH <sub>2</sub> -	0.000
04	-CH <sub>3</sub> &-CH=	-19.867	13	Bt &> CO <sub>2</sub>	0.000
05	-CH <sub>3</sub> &>C=	-54.090	13	Bt &-N--	-102.83
06	-CH <sub>3</sub> &-CO-	45.443	5		5
07	-CH <sub>3</sub> &-CO <sub>2</sub> -	-48.703	14	Bt &Cl-	0.000
08	-CH <sub>3</sub> &-O-	-39.941	14	Bt &I-	174.34
			4		4
			14	Bt &Br-	27.058
			2		

09	-CH <sub>3</sub> &>Si<	-1.855
10	-CH <sub>3</sub> &>B<	0.000
11	-CH <sub>3</sub> &-SO <sub>2</sub> <sup>-</sup>	-33.256
12	-CH <sub>3</sub> &-SO <sub>3</sub> <sup>-</sup>	-46.820
13	-CH <sub>3</sub> &-SO <sub>4</sub> <sup>-</sup>	0.000
14	-CH <sub>2</sub> - &-CH <sub>2</sub> -	0.437
15	-CH <sub>2</sub> - &>CH-	-25.526
16	-CH <sub>2</sub> - &>C=	0.000
17	-CH <sub>2</sub> - &-CH=	59.218
18	-CH <sub>2</sub> - &-C ≡	0.000
19	-CH <sub>2</sub> - &>C<	18.455
20	-CH <sub>2</sub> - &-Cl	39.592
21	CH <sub>2</sub> - &-F	24.085
22	CH <sub>2</sub> - &-CO <sub>2</sub> <sup>-</sup>	0.026
23	CH <sub>2</sub> - &-O-	1.882

14	3	Bt &- SO <sub>3</sub>	14.498
14	4	Bt &SO <sub>4</sub> <sup>-2</sup>	0.000
14	5	Bt &>P<	50.755
14	6	Bt &>B<	11.875
14	7	1,2,3-Taz &3-C H <sub>3</sub>	136.90 8
14	8	1,2,3-Taz &3-C H <sub>2</sub>	82.816
14	9	1,2,3-Taz &3=C H-	0.000
15	0	1,2,3-Taz &1-NH <sub>2</sub>	0.000
15	1	1,2,3-Taz &N <sub>3</sub> <sup>-</sup>	-36.000
15	2	1,2,3-Taz &NO <sub>3</sub> <sup>-</sup>	0.000
15	3	1,2,4-Taz &1-H	145.71 2
15	4	1,2,4-Taz &4 H	28.298
15	5	1,2,4-Taz &1-CH <sub>3</sub>	113.27 0
15	6	1,2,4-Taz &4-CH <sub>3</sub>	39.283
15	7	1,2,4-Taz &5 -CH <sub>3</sub>	-4.830

24	CH <sub>2</sub> - &-CO-	-7.999	15	1,2,4-Taz &1 - CH <sub>2</sub>	73.470
25	CH <sub>2</sub> - &-CN	-4.387	15	1,2,4-Taz &2 - CH <sub>2</sub>	0.000
26	CH <sub>2</sub> - &-N <sub>3</sub>	-11.856	16	1,2,4-Taz &4- CH <sub>2</sub>	18.947
27	CH <sub>2</sub> - &Bz	45.942	16	1,2,4-Taz &3- >C<	0.000
28	CH <sub>2</sub> - &Br	0.000	16	1,2,4-Taz &1 -CO	0.000
29	CH <sub>2</sub> - &Fc	6.310	16	1,2,4-Taz &1 - NH <sub>2</sub>	127.250
30	CH <sub>2</sub> - &- SO <sub>4</sub> <sup>-</sup>	-90.424	16	1,2,4-Taz &2 - NH <sub>2</sub>	0.000
31	CH <sub>2</sub> - &- SO <sub>2</sub> <sup>-</sup>	43.019	16	1,2,4-Taz &3 - NH <sub>2</sub>	0.000
32	CH <sub>2</sub> - &- SO <sub>3</sub> <sup>-</sup>	-11.586	16	1,2,4-Taz &4 - NH <sub>2</sub>	0.000
33	CH <sub>2</sub> - &- S -	2.251	16	1,2,4-Taz &5 - NH <sub>2</sub>	42.867
34	CH <sub>2</sub> - &>Si<	-1.184	16	1,2,4-Taz &>P<	0.000
35	CH <sub>2</sub> - &- PO <sub>3</sub> <sup>-</sup>	-43.265	16	1,2,4-Taz &5 -N <sub>3</sub>	-15.615
36	CH <sub>2</sub> &>C=	47.746	17	1,2,4-Taz &N <sub>3</sub> <sup>-</sup> or 3 - N <sub>3</sub>	-19.363
37	CH <sub>2</sub> - &>B<	-26.956	17	1,2,4-Taz &ClO <sub>4</sub> <sup>-</sup>	-6.891
38	>CH- &>CH-	-26.281	17	1,2,4-Taz &>B<	-33.186

39	>C< or >C- & - >CH-	-11.154	17	1,2,4-Taz&I-	21.886
40	>CH- & >C=	0.000	17	1,2,4-Taz&Br-	49.220
41	>CH- & -O	-26.447	17	1,2,4-Taz&-SO <sub>3</sub> <sup>-</sup>	77.818
42	>CH- & -SO <sub>3</sub> <sup>-</sup>	0.000	17	1,2,4-Taz&-N--	-73.790
43	>CH-- & -CO-	-12.103	17	1,2,4-Taz & NO <sub>3</sub> -	8.875
44	>CH- or >CH- & -CO <sub>2</sub> <sup>-</sup>	20.865	17	1,2,4-Taz & lmi-	0.000
45	>CH- & -NO <sub>2</sub>	0.000	17	1,2,4-Taz & tet	0.000
46	>CH- & >B<	0.000	18	Py & 2-Py	0.000
47	>CH- & F-	-10.559	18	Py & -1-CH <sub>3</sub>	0.000
48	>CH- & Br-	155.605	18	Py & 2-CH <sub>3</sub>	0.000
49	>C<&>C<	-4.510	18	Py & 3-CH <sub>3</sub>	-23.575
50	>C<&Br	0.000	18	Py & 4-CH <sub>3</sub>	-27.536
51	>C<&>B<	-45.000	18	Py & 1-CH <sub>2</sub>	15.923
52	>C<&>P<	-42.955	18	Py & -2-CH <sub>2</sub>	0.000
53	>C< or >C- & -SO <sub>2</sub> <sup>-</sup>	-0.746	18	Py & -3-CH <sub>2</sub>	-98.989

54	$>C<\&-NO_2^-$	1.306	18	Py $\&-4-CH_2$	0.000
55	$>C<\&-SO_4^-$	0.000	18	Py $\&> CO_2$	7.884
56	$>C<\&-SO_3^-$	-56.673	19	py $\&Cl^-$	139.125
57	$>C<\&-CO-$	10.709	19	py $\&Br^-$	160.406
58	$>C<\&-CO_2^-$	31.442	19	py $\&-N^-$ -or N	16.248
59	$>C<\&-F$	3.422	19	py $\&>P<-$	128.526
60	$>C- \&-CN$	0.000	19	py $\&>B<-$	62.398
61	HC= $\&-HC=$	78.774	19	py $\&PO_4^{-3}$	92.889
62	HC= $\&>C=$	0.000	19	py $\&SO_4^{-2}$	0.000
63	HC= $\&-NO_2$	0.000	19	S $\&-CH_3$	85.490
64	HC= $\&-CO$	0.000	19	S $\&-CH_2$	70.111
65	HC= $\&-CO_2$	0.000	19	S $\&N-$	-199.430
66	HC= $\&H_2C=$	0.000	20	S $\&>B<$	0.000
67	$>C= \&> C=$	0.000	20	N $\&-H$	21.404
68	$>C= \&S-$	0.000	20	N $\&-CH_3$	13.938

69	>C= &-F	0.000
70	>C= &-CN	0.000
71	>C= &-SO <sub>3</sub>	0.000
72	C H ≡ &-C ≡	0.000
73	H &-O-	73.121
74	H &-CO <sub>3</sub> <sup>-</sup>	0.000
75	H &-CO <sub>2</sub> <sup>-</sup>	7.192
76	H &-PO <sub>4</sub> <sup>-</sup>	21.404
77	H &-S-	0.000
78	H &-SO <sub>3</sub> <sup>-</sup>	0.000
79	H &-SO <sub>4</sub> <sup>-</sup>	-73.187
80	H- &>B<	-19.489
81	BZ &2-CH <sub>3</sub> -	0.000
82	BZ &3-CH <sub>3</sub> -	-13.885

20	3 N et -CH <sub>2</sub> -	9.847
20	4 N &>C=	0.000
20	5 N &>CH-	30.325
20	6 N &>Co<	0.000
20	7 N &-CN	0.000
20	8 N or -N <sup>-</sup> &>CO	-110.404
20	9 N &-Bz	-8.126
21	0 N &-Taz	0.000
21	1 N &Cl-	121.977
21	2 N &ClO <sub>4</sub> <sup>-</sup>	88.028
21	3 N &-N <sup>-</sup>	3.324
21	4 N &-I	78.153
21	5 N &-Br	69.617
21	6 N &>B< -	68.403

83	BZ & 4-CH <sub>3</sub> -	20.242
84	BZ & >C<	2.451
85	BZ & -O-	0.000
86	BZ & -CO-	134.799
87	BZ & -CO <sub>2</sub> <sup>-</sup>	45.877
88	BZ & -F	0.000
89	BZ & -Si	0.000
90	BZ & -S	0.000
91	BZ & -SO <sub>2</sub>	0.000
92	BZ & -SO <sub>3</sub> <sup>-</sup>	-41.485
93	O- & -C =S	0.000
94	SO <sub>2</sub> <sup>-</sup> & -Cl	0.000
95	SO <sub>2</sub> <sup>-</sup> & -F-	-4.685
96	S- & -C =S	52.279
97	S & -Ni	0.000

21	N & NO <sub>3</sub> <sup>-</sup>	37.384
21	8 -N-- & -NO <sub>2</sub>	0.000
21	9 -N- & -SO <sub>2</sub>	-8.387
22	0 N or - N- & -SO <sub>3</sub> <sup>-</sup>	121.336
22	1 N & >>P<-	86.707
22	2 N & -PO <sub>4</sub> <sup>-</sup>	0.000
22	3 N & -S-	0.000
22	4 N & C=S	0.000
22	5 N & SO <sub>4</sub> <sup>-2</sup>	71.148
22	6 N- & -CO-	10.557
22	7 N & -CO <sub>2</sub> <sup>-</sup>	-10.238
22	8 N & -CO <sub>3</sub> <sup>-</sup>	0.000
22	9 N & >C-- et >C<	9.145
23	0 guan & -CH <sub>3</sub>	15.546
23	1 guan & -CH <sub>2</sub> -	-4.672

98	S- &-CN	41.765	23	Guan &H-	-41.770
99	Si &-O	0.000	23	Guan &ClO <sub>4</sub> <sup>-</sup>	75.630
100	>B<&Bz	-3.211	23	Guan &Cl-	0.000
101	>B<&-F	3.046	23	Guan &-NO <sub>3</sub>	48.603
102	Co &-S	0.000	23	Guan &-N <sup>-</sup>	-21.113
103	Co &-CO	0.000	23	Guan &>B<-	0.000
104	tet &-NO <sub>2</sub>	25.228	23	Guan &-SO <sub>3</sub> <sup>-</sup>	0.000
105	lmi &-NO <sub>2</sub>	6.312	23	Guan &>P<-	0.000
106	triaz &- O-	0.000	24	Guan &-CO <sub>2</sub> <sup>-</sup>	0.000
107	furan &-CO	31.997	24	Guan &-S-	0.000
108	thiophene &-CO	31.731	24	>P<&-CH <sub>3</sub>	30.142
109	(Ph) <sub>3</sub> &- O	9.660	24	>P<&-CH <sub>2</sub> -	19.282
110	mom &- O	-6.301	24	>P<&Cl	50.216
111	IM &2-CH <sub>2</sub>	59.220	24	>P<&>B<	-11.881
112	IM &2-CH <sub>3</sub>	48.967	24	>P<&Br	21.344



11 3	IM &2-IM or IM+	21.449
11 4	IM &4-CH <sub>3</sub>	80.429
11 5	IM &5-CH <sub>3</sub>	-17.576
11 6	IM &Cl-	110.120
11 7	IM &Br- or -Br	97.354
11 8	IM & I- ou -I	126.982
11 9	IM &-N--	7.538
12 0	IM &- S-	-7.985
12 1	IM &- SO <sub>3</sub> -	108.409
12 2	IM &- SO <sub>4</sub> -	81.675
12 3	IM &>B< -	54.019
12 4	IM &NO <sub>3</sub> <sup>-</sup>	61.296
12 5	IM &NO <sub>2</sub> <sup>-</sup> or -NO <sub>2</sub>	107.809
12 6	IM &>P<-	78.450
12 7	IM &-CO <sub>2</sub> <sup>-</sup>	6.135

24 7	>P<&-F	0.217
24 8	>P<&Bz	41.235
24 9	>P<- &-N <sup>-</sup> -	-28.282
25 0	>P<- &-NO <sub>3</sub> <sup>-</sup>	0.000
25 1	>P<- &>P<	0.000
25 2	>P<- &-SO <sub>3</sub> <sup>-</sup>	0.000
25 3	>P<&-Ni -	0.000
25 4	>P<&-Co -	0.000
25 5	>P<&>C-	-38.039
25 6	>P<&-CO <sub>2</sub> <sup>-</sup>	0.000
25 7	>P<&-S-	0.000
25 8	>P<&Fe(CN) <sub>6</sub>	0.000
25 9	Tetaz &1-CH <sub>3</sub>	0.000
26 0	Tetaz &4-CH <sub>3</sub>	63.192
26 1	Tetaz &5-CH <sub>3</sub>	127.716

128	IM & N <sub>3</sub> <sup>-</sup>	0.000	262	Tetaz & 1-NH <sub>2</sub>	0.000
129	IM & >C-	52.458	263	Tetaz & 2-NH <sub>2</sub>	0.000
130	IM & WOF <sub>5</sub>	19.630	264	Tetaz & 5-NH <sub>2</sub>	0.000
131	IM & ClO <sub>4</sub>	45.574	265	Tetaz & I-	0.000
132	IM & AlCl <sub>4</sub>	34.776	266	Tetaz & NO <sub>3</sub> <sup>-</sup>	-0.036
133	IM & SbF <sub>6</sub>	0.000	267	Tetaz & -N-	0.000
134	IM & AsF <sub>6</sub>	92.780	268	Tetaz & ClO <sub>4</sub> <sup>-</sup>	0.000

Table 4: Second-order structural groups and their interaction and contributions

No	Interactions	$\Delta D_f$ / K	No	Interactions	$\Delta D_f$ / K
01	H- & IM & -H	22.968	09	>C<& IM & -CH <sub>3</sub> -	78.965
02	CH <sub>3</sub> - & IM & -H	47.444	10	>C<& IM & -CH <sub>2</sub> -	23.108
03	CH <sub>3</sub> - & IM & & CH <sub>3</sub> -	50.649	11	CH <sub>3</sub> - & Bt & -CH <sub>3</sub>	0.000
04	-CH <sub>2</sub> - & IM & -H	17.758	12	CH <sub>3</sub> - & Bt & -CH <sub>2</sub> -	149.661
05	CH <sub>3</sub> - & IM & -CH <sub>2</sub> -	10.754	13	CH <sub>2</sub> - & Bt & -CH <sub>2</sub> -	109.356
06	-CH <sub>2</sub> - & IM & -CH <sub>2</sub> -	30.225	14	-SO <sub>2</sub> - & -N- & -SO <sub>2</sub> -	12.795

07	>CH- & IM & - CH <sub>3</sub> -	-8.195	15	-NO <sub>2</sub> &-N- & - NO <sub>2</sub>	72.716
08	>CH- & IM & - CH <sub>2</sub> -	28.211	16	-CN & -N- & -CN	0.971

As shown in Figure 4 presenting the performance of the newly developed model, the latter is consistent with experimental data for a large portion of data points, although large discrepancies are observed for some  $T_m$  values as 68.51K. Such large deviations were also observed in similar studies as pointed out by Valderrama (2014) [9] who reported differences between experimental and predicted melting points as high as 180 K.

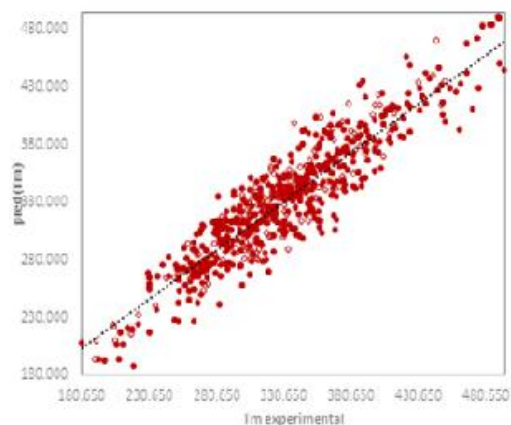


Figure 3: Comparison between experimental and predicted  $T_m$  data for the training set (●) and test set (○).

For a total of 684 experimental melting points, the average relative deviation (AARD) and correlation coefficient ( $R^2$ ) for this model were calculated as 5.04 % and 0.85 respectively, while the average absolute deviation between calculated and experimental data was 68.69 K. These values indicate an acceptable level of both accuracy and predictability. A further comparison is made in Table 5 between the performance of this model and that of other methods reported in the literature.

Table 5: Comparison between the model proposed in this study and those reported in the literature.

Mode	References	No.	$R^2$	Type of ILs	%
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-basis		ILs			AARD
QSP R	Katritzky et al. [10]	104	0.751	Imidazolium bromides	-
		45	0.689	benzimidazolium	-
	Steven Trohalaki and Pachter [11]	126	0.713	Pyridinium bromides	-
	Eike et al. [12]	75	0.790	Quaternary	-
		34	0.716	ammonium bromides	-
	Carrera and Aires-de-Sousa [13]	13	0.873	Triazolium bromide	-
		13	0.839	Triazolium nitrate	-
	Zhang et al. [3]	126	0.933	Pyridinium bromides	-
		126	0.822	Imidazolium tetrafluoroborate	-
	López-Martin et al. [14]	126	0.748	-	-
		16	0.904	-	-
		25	0.920	-	-
	Yan et al. [15]	62	0.869	-	-
		50	0.890		
	Natalia Kireeva et al [16]	288	0.810	diverse	17.75
	Natalia Kireeva et al. [17]	717	0.64 -0.85	Diverse	-
563		0.658	Diverse	7.3	
GC	Y. Ren et al. [18]	288	0.712	diverse	24.33
	J.A.Lazzús [19]	400	0.884	Diverse	7.07

Huo et al. [20]	190	0.898	Imidazolium benzimidazolium	5.86
C. Aguirre et al. [21]	136	-	Diverse	7.80
F. Gharagheizi et al. [22]	799	0.811	Diverse	5.82
Valderrama et al. [9]	667	-	Diverse	5.1
	297	-	Imidazolium	5.3
Keshavarz et al.[23]	195	0.857	imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, phosphonium-, and piperidinium	6.5
Valderrama et al. [24]	188	-	Imidazolium, ammonium, pyridinium, phosphonium, sulfonium, piperidinium, pyrrolidinium, triazolium	6.47
<b>this work</b>	<b>684</b>	<b>0.85</b>	<b>Diverse</b>	<b>5,04</b>

With respect to previous models, no improvement in either accuracy or predictability can be claimed from this present study. However, its merits are undoubtedly the extensive nature of the database used (the largest database in Table 6) as well as the ability to differentiate between isomers. The latter cannot be achieved with conventional group contribution methods. AARD between model predictions and experimental data is provided in Table 6 for all classes of ionic liquids contained in the database. It appears that the model developed in this study exhibits the best performance for imidazolium-based ionic liquids, which represent 43% of all investigated ILs. This can be regarded as significant, given the popularity of this class of ionic liquids. The worst results are those associated with butyrolactam-based ILs.

Table 6: Deviations between experimental and predicted melting temperatures for various classes of ILs

Class of ILs	Abbreviation	No of ILs	%AARD
Imidazolium	IM	230	5.25
Benzotriazolium	Bt	12	1.79
Triazolium	Taz	49	3.03
Pyridinium	py	41	4.66
Sulfonium	S	10	4.46
Ammonium	N	201	4.46
Piperidinium	PP	09	7.15
Pyrrolidinium	P <sub>n<sub>1</sub>n<sub>2</sub></sub>	38	5.35
Piperazinium	Pip n <sub>1</sub> n <sub>2</sub>	1	7.62
Caprolactam	NHC	3	3.17
Butyrolactam	PYor Az	1	11.15
Morpholinium	MO	19	4.91
Tetrazolium	Tetaz	7	1.76
Oxazolidinium	OX	06	2.92
Amino acids	AA	23	5.70
Guanidinium	Guan	12	3.75
Phosphonium	P	19	4.53
Pyrimidine	(R <sub>1</sub> R <sub>2</sub> )N=(R <sub>3</sub> R <sub>4</sub> )	11	7.44

Table 7: The statistical parameters for the developed model

	<i>Training set</i>	<i>Validation set</i>	<i>Overall</i>
R <sup>2</sup>	0.848	0.868	0.848
%AARD	5.22	4.55	5.04
Standard Deviation	68.69	59.32	68.69
No of ILs	505	179	664

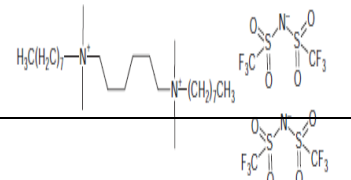
More insight into the performance of the new GIC model is given in the appendix as supplementary materials. These consist of a table presenting the calculated and experimental values for all 684 ionic liquids considered in this study. Additionally, a working example is provided to illustrate the use of the GIC model.

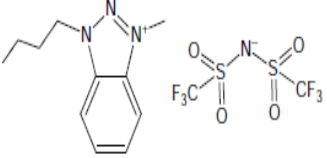
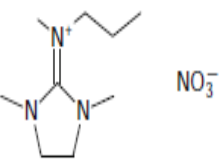
## Conclusion

Unlike conventional group interaction methods, the new approach presented in this study takes isomerism into account. A wide applicability range, acceptable accuracy, and good predictive ability represent its remarkable features. A wide applicability range is owed to the extensive database used, comprising altogether 1073 data points for 684 ionic liquids, as well as the variety of cations and anions involved in the modelling process. Acceptably low deviations between experimental values and those predicted in this study (AARD=5 %) coupled with a correlation coefficient of 0.85, suggest that the model is generally accurate and reliable. The developed model would be useful, among other things, for solid-liquid equilibrium calculations in the absence of experimental ILs' melting point data as well as for the development of process simulators.

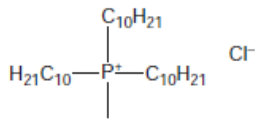
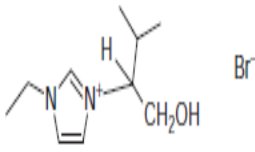
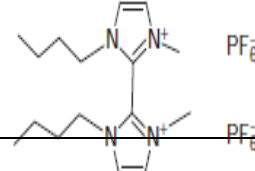
## Supplementary Materials

Table A. Worked example for *T<sub>m</sub>* prediction using the developed GIC model

Compound	P <sup>exp</sup> (K)	Interactions	Frequenc y	Contributi on
	324,1 5	-SO <sub>2</sub> - & -N <sup>-</sup> - & -SO <sub>2</sub> -	02	12.795

<p>N,N,N'-tetramethyl-N,N'-dioctyl-1,6-hexanediammonium di[bis(trifluoromethanesulfonyl)amide]</p>		CH <sub>3</sub> - & -CH <sub>2</sub> -	02	0.373		
		-CH <sub>2</sub> - & -CH <sub>2</sub> -	17	0.436		
		>C< or >C- & -SO <sub>2</sub> -	04	-0.745		
		>C<& -F	12	3.422		
		N & CH <sub>3</sub> -	04	13.938		
		N & -N-	02	3.324		
		N & -CH <sub>2</sub> -	04	9.847		
		E=2				
		T <sub>m</sub> <sup>cal</sup> (K) = 325.945				
 <p>1-Butyl-3-methyl benzotriazolium bis((trifluoromethyl)sulfonyl)imide</p>	302.15	CH <sub>3</sub> - & Bt & -CH <sub>2</sub>	01	149.661		
		-SO <sub>2</sub> - & -N- & -SO <sub>2</sub> -	01	12.795		
		>C< or >C- & -SO <sub>2</sub> -	02	-0.746		
		CH <sub>3</sub> - & -CH <sub>2</sub> -	01	0.373		
		CH <sub>2</sub> - & -CH <sub>2</sub> -	02	0.437		
		>C<& -F	.06	3.422		
		Bt & -N-	01	-102.835		
		E=1				
		T <sub>m</sub> <sup>cal</sup> (K) =302.15				
 <p>1,3-Dimethyl-2-(N-methyl-N-propyl)</p>	304.15	CH <sub>3</sub> & -CH <sub>2</sub> -	01	0.373		
		-CH <sub>2</sub> - & -CH <sub>2</sub> -	02	0.437		
		Guan & -CH <sub>2</sub> -	03	4.672		



ammonium)imidazolidine nitrate		Guan & CH <sub>3</sub> -	03	15. 546
		Guan & -NO <sub>3</sub> <sup>-</sup>	01	48. 603
		E=1		
		T <sub>m</sub> <sup>cal</sup> (K) = 304.71		
 Tridecylmethyl phosphonium chloride	372.0 5	CH <sub>3</sub> - & -CH <sub>2</sub> -	03	0.373
		-CH <sub>2</sub> - & -CH <sub>2</sub> -	24	0.437
		P & -CH <sub>2</sub> -	03	19.282
		P & CH <sub>3</sub> -	01	30.142
		P & Cl-	01	50.216
		E=1		
		T <sub>m</sub> <sup>cal</sup> (K) = 372.05		
 L-1-Ethyl-3-(1'-hydroxy-3'- methyl-2'-butanyl) imidazolium bromide	284.1 5	>CH- & IM & -CH <sub>2</sub> -	01	28.211
		CH <sub>3</sub> - & -CH <sub>2</sub> -	01	0.373
		CH <sub>3</sub> - & >CH-	02	26.566
		-CH <sub>2</sub> - & -O-	01	1.882
		-CH <sub>2</sub> - & >CH-	01	-25.525
		H- & -O-	01	73.121
		>CH- & >CH-	01	-26.280
		IM & Br- Or -Br	01	97.353
		E=1		
		T <sub>m</sub> <sup>cal</sup> (K) = 296.992		
 PF <sub>6</sub> <sup>-</sup>	348.1 50	CH <sub>3</sub> - & IM & -CH <sub>2</sub> -	02	10.754
		CH <sub>3</sub> - & -CH <sub>2</sub> -	02	0.373

1,1'-Dibutyl-3,3'-dimethylimidazolium bis(hexafluorophosphate)	-CH <sub>2</sub> - & -CH <sub>2</sub> -	04	0.437
	IM & 2-IM or IM+	01	21.449
	IM & P	02	78.450
	P & -F	12	0.217
	E=2		
	T <sub>m</sub> <sup>cal</sup> (K) = 357.28		

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