



Predicting the melting temperature and the heat of melting of ionic liquids

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ABSTRACT

The group contribution concept is used and a simple and general method is proposed for estimating phase change properties of ionic liquids. The proposal includes some especial characteristics, such as: (i) the model considers the well-known relation between the melting temperature, the heat of melting, and the entropy of melting; (ii) the model considers that a given group has a contribution value if the group occurs in the cation and another different value if it occurs in the anion; and (iii) the correlation process considers experimental data of melting temperature and heat of melting. Despite its simplicity, the proposed model provides deviations that are similar to other more sophisticated, multiparametric models. The literature analysis and our own results indicate that there are still some unknown facts that determine phase transitions and that models have not been able to include and quantify. All this indicates that the goal of having the most general and accurate model for predicting the melting temperature and melting enthalpy of ionic liquids is still far away. However, the present proposal represents a new attempt for contributing to this interesting puzzle of getting good and reasonable estimates for the melting properties which could help in choosing the appropriate ionic liquid for an existing or new application.

1. Introduction

In a paper published at the beginnings of 2014 by one of the authors (Valderrama, 2014), arguments related to the reasons why not having at that time enough information for developing an accurate method for estimating the melting temperature (T_m) of ionic liquids were presented. In that paper the author stated that *"it is a myth that with the present data we can obtain better and generalized correlations and estimation methods for the melting temperature of ILs, at least in the way done until now"*. As analyzed by the author, values of the melting temperature of ionic liquids reported in the literature present great discrepancies, errors that are propagated to the correlation results. Despite this, the author indicated that until 2014 some progress had been done in determining experimental melting temperature values and in developing methods for their estimation, although new approaches were frequently published. Then, he discussed the main four methods that had been used for estimating melting temperature of ionic liquids: chemical homology (ChemH), group contribution methods (GCM), quantitative structure- property relationship (QSPR), and artificial neural network (ANN).

Seven years have passed since that contribution of 2014 mentioned above and some few papers about correlating and estimating the melting temperature of ionic liquids (ILs) have been published since then. These contributions follow the same ideas published before 2014, so in

that sense not much progress has been done. For instance, Mehrkesh and Karunanithi (Mehrkesh and Karunanithi, 2016) developed an empirical correlation using different types of molecular descriptors based on the cation and anion radii, density of ionic liquids, mass of the cation, and the dielectric energy of the anion. These authors applied their model to a limited quantity of ionic liquids (37) and reported maximum relative deviation below 10%. Quill et al. (3) applied a neural-fingerprinting architecture algorithm based on smiles strings of the anion and cation for melting temperature estimation. The results show a coefficient of determination around 0.64 and maximum deviations of 40%. Keshavarz et al. (Keshavarz et al., 2018) developed an empirical correlation based on multiple linear regression. The new correlation depends on different molecular descriptors of the anion and the cation. The model also includes the number of carbons, hydrogen, and nitrogen atoms for the cation and the number of hydrogens, nitrogen, bromine, chlorine, and aluminum atoms for the anion. The mean absolute relative deviation is below 7.5% when is applied to estimate the melting temperature of 243 ionic liquids, but in fact maximum deviations of 91.2K (43%) are reported. Venkatraman et al. (Venkatraman et al., 2018) developed a machine learning framework using a cubist, random forest, and gradient boosted regression for melting temperature estimation. The model is compared with quantum chemistry estimations based on COSMOtherm and the results show that the model described the melting temperature

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Notation**Symbols**

H	Heat of melting in kJ/mol
M	Molar mass (g/mol)
n	Number of times that a group appears in a molecule
N	Number of data
np	Number of adjustable parameters of the model
ns	Number of ionic liquids considered
T	Temperature (K)

Abbreviations

AARD	Average absolute relative deviation
ARD	Average relative deviation
ANN	Artificial neural network
DDB	Dortmund Databank
GCM	Group contribution method
IL	Ionic liquid
MAD	Maximum absolute relative deviation
MS	Microsoft
NA	Not applicable
NIST-ILs	National Institute of Standards and Technology - Ionic Liquids Database
QC	Quantum chemistry
QSPR	Quantitative structure property relationships

Greek letters

α, β, γ	Constant parameters in Eq. (4): $\Delta S_m = \alpha + \beta \cdot M_c + \gamma \cdot M_a$
ΔH_m	Contribution to the heat of melting in kJ/mol
ΔS_m	Entropy of melting in kJ/mol•K

Super/subscripts

a	Anion
c	Cation
cal	Calculated
exp	Experimental
i	Group i for the GCM
m	Melting
mo	Constant parameter associated to the heat of melting
max	Maximum value

with a determination coefficient above 0.65 and maximum deviations of 50K (about 20%). Cerecedo-Cordoba et al. (2019) analyzed a data set of 415 imidazolium ionic liquids using QSPR techniques. These authors use clustering techniques to improve melting temperature estimations and report mean absolute relative deviation lower than 6.4% and maximum deviations of 32%. More recently, these same authors developed new neuroevolutionary trained neural networks for correlating and testing melting temperature (Cerecedo-Cordoba et al., 2020). In total, 155 imidazolium-type ionic liquids are evaluated and present a mean absolute relative deviation during training of around 5.7% and 8.4% during testing, with maximum deviations of 57%. To the best of the authors' knowledge, the most recent paper about the use of group contributions for estimating the melting temperature of ionic liquids is that of Chen et al. (Chen et al., 2019). These authors proposed a 22-parameter model and use 225 ionic liquid data of T_m to determine the model parameters. The authors report an average absolute relative deviation of 7.1% with maximum deviation around 20%. During testing, deviations up to 50 K are observed.

In group contribution methods, the property of a compound is calculated by summing up the contributions of certain defined groups of atoms, considering at the same time the number frequency of each group occurring in the molecule. In some way, the concept of group contribution involves some structural information by defining certain groups and their quantity occurring in a substance and it also includes the size, defined by the mass of the groups. Several authors have applied

Table 1

The 47 groups for the anion and for the cation considered in the proposed GCM.

	Non-ring	18	=O (any_other)		Aromatics
1	-CH3	19	-NH2	34	-CH2-
2	-CH2-	20	-NH3	35	>CH-
3	>CH-	21	-NH-	36	=CH-
4	>C<	22	>N-	37	>C<
5	=CH2	23	=N-	38	=C<
6	=CH-	24	-CN	39	-O-
7	=C<	25	-NO2	40	-OH (phenols)
8	=C=	26	-F	41	>C=O
9	=(-)CH	27	-Cl	42	-NH-
10	=(-)C-	28	-Br	43	>N-
11	-OH	29	-I	44	=N-
12	-O-	30	-P		Metals
13	>C=O	31	-B	45	Al
14	-CHO	32	-S-	46	As
15	-COOH	33	O=S=O	47	Fe
16	-COO-				
17	-HCOO-				

group contributions for estimating some properties of ILs using different groups for the same molecule depending on the property being estimated (Coutinho et al., 2012). In applying group contribution, one implicitly accepts the fact that, since we do not know the correct division of groups (if there is any), definition of groups is more or less an arbitrary matter. Not less important is the fact that these methods have the advantage of quick estimates without requiring sophisticated computational calculations that usually need information which is not readily available.

The proposal presented here is a new attempt for contributing to this interesting puzzle of getting good and reasonable estimates for the melting temperature which could help in defining new applications for ionic liquids or choosing the appropriate ionic liquid for a given existing application. The proposed model consists of using a simple group contribution method, but which includes some special characteristics: (i) it is simple to apply; (ii) it differentiates the contribution of a given group depending on whether it is present in the cation or the anion; (iii) it has a sound thermodynamic basis; (iv) it can be used for different types of ionic liquids; and (v) extension to new ionic liquids can be easily done.

2. Group contribution methods

One of the simplest group contribution method (GCM) for estimating the melting temperature of organic substances is that of Joback and Reid (Joback and Reid, 1987) who proposed a linear relation between T_m and the values of the contributions. The Joback-Reid model is defined as:

$$T_m = 122.5 + \sum n_i \Delta T_{m,i} \quad (1)$$

In Eq. (1), n_i is the number frequency of each group "i" occurring in the molecule and $\Delta T_{m,i}$ is the contribution of each group "i" to the melting temperature.

The groups defined for the group contribution method presented in this work are the same as those defined by the authors in a previous publication related to the estimation of critical properties (Valderrama et al., 2019) and summarized in Table 1. One especial change is incorporated in the present method: if a given group is present in the anion and in the cation, it is not assumed that they have the same contribution value, so the groups are treated differently. For instance, for the ionic liquid [trimethylbutylammonium] bis[(trifluoromethyl)sulfonyl]imide the group [>N-] appears once in the cation and once in the anion so the contributions to be calculated will be different; one value is assigned for the group present in the anion [$>N^-$]_{anion}, and a different value is assigned for the group present in the cation [$>N^-$]_{cation}. Also, for determining the values of the contributions, both the experimental values of the melting

temperature and for the melting enthalpy are considered, as explained in a forthcoming section.

3. Methodology

To develop a simple and reliable model for correlating and estimating the melting temperature of ionic liquids, the following methodology was adopted: i) formulation of the model based on well-founded theoretical basis (relation between T_m and the heat of melting and the entropy of melting); ii) identification of the type of data needed for determining the model parameters (mass of the cation, mass of the anion, melting temperature, melting enthalpy, and the groups forming the ionic liquid); iii) identification of the most acceptable sources for the data needed (National Institute of Standards and Technology database NIST-ILs (Kazakov et al., 2013, Dong et al., 2007) and Dortmund databank DDB (DDB 2013); iv) defining the data for developing the model and data for testing the model (NIST-ILs for determining the model, and DDB for testing the predictive capabilities of the model); v) choosing a numerical technique and software selection for determining the model parameters (by minimizing the difference between calculated and experimental data using MS Excel with the Solver tool); vi) determining the model parameters and estimate the deviations of the calculated values of T_m with respect to experimental values (determining the relative and absolute deviations); and vii) predicting T_m of the ionic liquids not used during the obtention of the model parameters (analyzing the deviations between predicted values and experimental data from the DDB).

3.1. Melting temperature model

As indicated above, the proposed model is developed based on the well-founded theoretical relation between the melting temperature (T_m), the heat of melting (ΔH_m), and the entropy of melting (ΔS_m) as shown in Eq. (2):

$$T_m = \frac{\Delta H_m}{\Delta S_m} \quad (2)$$

In Eq. (2), ΔH_m is in [kJ/mol] and ΔS_m is in [kJ/mol•K] and each of these terms are treated differently to express their contributions in the most reasonable way. The enthalpy of melting depends on the interactions between the molecular fragments of the cation and anion, and it is usually assumed to be a linear combination of the contributions of each of these fragments or groups (Chickos and Nichols, 2001, Valderrama and Campusano, 2016, Zhu et al., 2009, Keshavarz et al., 2016). Thus, the following relation is used for ΔH_m in the proposed group contribution method:

$$\Delta H_m = H_{mo} + \sum [n_{ic} \Delta H_{m,ic}] + \sum [n_{ia} \Delta H_{m,ia}] \quad (3)$$

In Eq. (3), n_{ic} is the number frequency of each group "i" occurring in the cation and $\Delta H_{m,ic}$ is the contribution to the enthalpy of melting of each group "i" present in the cation. Similarly, n_{ia} is the number frequency of each group "i" occurring in the anion and $\Delta H_{m,ia}$ is the contribution to the melting enthalpy of each group "i" present in the anion. The term H_{mo} is a constant for all ionic liquids.

For the entropy of melting, several authors have indicated that this property depends on structural characteristics. Dannenfelser et al. (Dannenfelser and Yalkowsky, 1996) 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, while Zhao and Yalkowsky (Zhao and Yalkowsky, 1999) stated that the entropy of melting ΔS_m is mainly determined by the change in rotational and conformational freedom. In another approach, Sánchez-Soto et al. (Sánchez-Soto et al., 2002) showed that for polymers, there was a simple linear relation between the melting entropy and the molar mass of the polymer. Other authors have used this fact for correlating the entropy of melting with the size of chemical families of ionic liquids such as $[C_n\text{mim}][\text{bti}]$, $[C_n\text{mim}][\text{PF}_6]$

Table 2

Ionic liquids included in the NIST database that present variable differences in the reported melting temperature.

N°	ionic liquid name	number of data	Max. diff T_m
1	[N4444] [Cl]	7	51.0
2	[NHHH2] [Ac]	2	39.5
3	[N4444] [TMEM]	2	37.0
4	[deim] [bti]	2	35.5
5	[C4mim] [Cl]	16	28.9
6	[C2mim] [bti]	17	21.9
7	[P14] [bti]	15	17.1
8	[NHHH3] [HCO2]	2	16.0
9	[C2mim] [Cl]	9	11.7
10	[C2mim] [tcc]	2	11.1
11	[C2mim] [BF4]	9	10.5
12	[C6mim] [bti]	10	10.2
13	[C10mim] [Cl]	2	9.1
14	[C7mim] [bti]	2	7.9
15	[bpy] [BF4]	2	7.8
16	[C2mim] [Br]	5	7.1
17	[C4mim] [TfO]	5	6.1
18	[C12mim] [BF4]	2	5.9

and $[C_n\text{mim}][\text{Br}]$ (Shimizu et al., 2009, Rodrigues and Santos, 2016). We have also considered the mass of the ionic liquid as a structural parameter, separating the contributions of the mass of the cation and the mass of the anion (M_c , M_a). The proposed mathematical representation for ΔS_m is:

$$\Delta S_m = \alpha + \beta M_c + \gamma M_a \quad (4)$$

In Eq. (4), α , β and γ are constant values for all ionic liquids, M_c and M_a are the mass of the cation and of the anion, respectively. Substituting Eqs. (3) and (4) into Eq. (2), the model to estimate the melting temperature of ILs is:

$$T_m = \frac{H_{mo} + \sum [n_{ic} \Delta H_{m,ic}] + \sum [n_{ia} \Delta H_{m,ia}]}{\alpha + \beta M_c + \gamma M_a} \quad (5)$$

Finally, the model for the melting temperature contains four constants for all ionic liquids, and specific values of $\Delta H_{m,i}$ for the groups defined in the group contribution method. The value of the constants and of the contributions are determined from experimental data of melting temperature and heat of melting of ionic liquids.

3.2. Literature data

Experimental data on melting temperature and heat of melting were gathered from the NIST-ILs database (Kazakov et al., 2013, Dong et al., 2007). This database operates online and collects experimental data of several physical and transport properties of ionic liquids. The database also reports the uncertainty of the values provided by the authors (Valderrama and Campusano, 2016, Valderrama and Rojas, 2012).

Of all the cases in which various data were available, the average difference between the highest and the lowest experimental data reported by the NIST database is 5.9 K, with a maximum of 51 K, as seen in Table 2. This large difference corresponds to tetrabutylammonium chloride. For this substance, Lapidus et al. (Lapidus et al., 2006) reported a value of 314 K. In the same NIST database, Elias and Strecher (Elias and Strecher, 1966) gave a value of 365.1 K for the same ionic liquid. Another example of high discrepancy is ethyl ammonium acetate (the second IL in Table 2). Burrell et al. (Burrell et al., 2010) reported a value of 320.6 K while Greaves et al. (Greaves et al., 2006) gave a value of 360.1 K, presenting a difference of around 40 K. These and other large discrepancies shown in Table 2 between experimental data for the same ionic liquid do not help in formulating good, robust models. In the Table, the number of experimental data for each of the ionic liquids is listed in the third column. In the last column, the difference between the highest and the lowest experimental value reported in the

NIST-ILs database is presented (Kazakov et al., 2013, Dong et al., 2007). In this work, if the difference between the highest and lowest reported values was greater than 10 K, the ionic liquid was not considered in the analysis (Valderrama and Campusano, 2016, Valderrama and Rojas, 2012). Finally, a total of 124 values of melting temperature and 28 values of heat of melting of ionic liquids were collected from the NIST-ILs database, including all types of ionic liquids. For each ionic liquid only one value of T_m and one value of ΔH_m were used.

Another source for data on melting temperature of ionic liquids is the Dortmund Databank (DDB 2013). From these data we selected those values which correspond to ionic liquids that were not included in the NIST-ILs database (Kazakov et al., 2013, Dong et al., 2007) and therefore were not used in obtaining the model parameters. In this way, prediction can be truthfully done. Thirteen ionic liquids available in the DDB were different from those of the NIST-ILs database which were used for developing the model and determining the model parameters. Once the model was developed, the same model with the same values of the parameters was used for estimating the melting temperature of the 13 ionic liquids without any other fitting or the use of any other parameter.

3.3. Data treatment

As described above, the data compiled by the NIST database (Kazakov et al., 2013, Dong et al., 2007) were chosen for obtaining experimental data for the temperature and the enthalpy of melting of ionic liquids (124 experimental for the melting temperature and 28 values for the enthalpy of melting).

The objective function to be minimized was defined in terms of the average absolute deviations (AARD) for the melting temperature and for the melting enthalpy, as shown in Eq. (6):

$$AARD = \frac{100}{N_{T_m}} \sum_{i=1}^{N_{T_m}} \left| \frac{T_{m,i}^{cal} - T_{m,i}^{exp}}{T_{m,i}^{exp}} \right| + \frac{100}{N_{\Delta H_m}} \sum_{i=1}^{N_{\Delta H_m}} \left| \frac{\Delta H_{m,i}^{cal} - \Delta H_{m,i}^{exp}}{\Delta H_{m,i}^{exp}} \right| \quad (6)$$

In Eq. (6), N_{T_m} is the number of melting temperature data, $N_{\Delta H_m}$ is the number of melting enthalpy data, T^{exp} and T^{cal} represent the experimental and calculated values of the melting temperature and ΔH_m^{exp} and ΔH_m^{cal} represent the experimental and calculated values of the melting enthalpy.

The fitting procedure is done using Excel's built-in Solver. The objective function and the optimization method have been successfully used in the literature to adjust the parameters of physicochemical models (Walsh and Diamond, 1995, Kemmer and Keller, 2010). Finally, the optimum values for the constants of the model and of the contributions were determined and are presented in Table 3.

4. Results and discussion

Once the model parameters are estimated by minimizing the difference between experimental and calculated values of T_m and ΔH_m , expressed through the absolute average relative deviation (AARD of Eq. 6), two other statistical parameters are analyzed: the average relative deviation (ARD), and the maximum absolute deviation (MAD), parameters that can truly establish the accuracy of a model (Valderrama and Alvarez, 2005):

$$ARDT_m = \frac{100}{N_{T_m}} \sum_{i=1}^{N_{T_m}} \frac{T_{m,i}^{cal} - T_{m,i}^{exp}}{T_{m,i}^{exp}} \quad (7)$$

$$ARD\Delta H_m = \frac{100}{N_{\Delta H_m}} \sum_{i=1}^{N_{\Delta H_m}} \frac{\Delta H_{m,i}^{cal} - \Delta H_{m,i}^{exp}}{\Delta H_{m,i}^{exp}} \quad (8)$$

$$MADT_m = \max \left| \frac{T_{m,i}^{cal} - T_{m,i}^{exp}}{T_{m,i}^{exp}} \right| \quad (9)$$

Table 3

Values of the cation and anion group contributions for the proposed model. *: indicates that the group is not included in the cation contribution values.

without rings			
Group	M_i (g/mol)	Cation contribution $\Delta H_{m,ic}$ (kJ/mol)	Anion contribution $\Delta H_{m,ia}$ (kJ/mol)
-CH3	15.035	1.7310	1.5040
-CH2-	14.027	0.9808	0.4229
>CH-	13.019	0.7435	-0.0359
>C<	12.011	2.3858	0.7978
=CH2	14.027	1.2630	-1.2514
=CH-	13.019	1.1151	-0.3161
=CH-	12.011	-0.1434	-0.1434
=C=	12.011	0.3325	3.6680
=(-)CH	13.019	-1.7431	-1.7431
=(-)C-	12.011	3.6680	3.6680
-OH	17.008	3.1287	1.4754
-O-	16.000	1.3256	0.3047
>C=O	28.011	3.4444	3.4444
-CHO	29.019	1.7028	1.7028
-COOH	45.018	8.5964	8.5964
-COO-	44.010	2.8997	1.6170
HCOO-	45.018	10.2030	-0.0649
=O(other)	16.000	-0.7928	-0.7928
-NH2	16.023	4.6890	3.8522
-NH3	17.031	0.8072	4.0673
-NH-	15.015	2.8324	2.8324
>N-	14.007	0.5764	-0.0033
=N-	14.007	0.3478	1.5404
-CN	26.018	3.2063	-0.0373
-NO2	46.006	1.8123	1.7907
-F	18.999	2.5688	0.7498
-Cl	35.453	0.0293	1.7157
-Br	79.904	2.1708	5.4581
-I	126.905	2.0461	3.9280
-P	30.974	0.4230	0.9264
-B	10.811	-1.8219	-1.5051
-S-	32.066	0.3026	0.5763
-SO2	64.065	4.3331	1.5936
with rings			
-CH2-	14.027	0.2990	-0.3864
>CH-	13.019	0.4830	0.4830
=CH-	13.019	1.3369	3.7121
>C<	12.011	3.3692	3.3692
=C<	12.011	2.1579	-5.4406
-O-	15.9995	0.7102	0.7102
-OH	17.0075	4.9803	4.9803
>C=O	28.0105	4.4901	4.4901
-NH-	15.015	1.8753	1.8123
>N-	14.007	0.2726	1.5968
=N-	14.007	0.1265	1.4521
Al	26.982	*	0.2990
As	74.922	*	5.3917
Fe	55.847	*	0.3238

$$\alpha = 9.7736 \cdot 10^{-3}; \beta = 2.4599 \cdot 10^{-4}; \gamma = 1.4582 \cdot 10^{-4}; H_{mo} = 3.8315$$

$$MAD\Delta H_m = \max \left| \frac{\Delta H_{m,i}^{cal} - \Delta H_{m,i}^{exp}}{\Delta H_{m,i}^{exp}} \right| \quad (10)$$

Table 4 summarizes the results, including the deviations defined above (Eqs. 7–10), and other information that show the accuracy of the model. As observed in this table, the overall absolute average relative deviation ($AARDT_m$) during the correlation procedure is 6.47% (with maximum deviation $MADT_m$ of 15.89%), and the absolute average deviation ARD is 0.03%. On the other hand, $AARDT_m$ and $ARDT_m$ for the prediction step are 6.93% and 4.40% (with $MADT_m$ of 16.36%), respectively. For all ionic liquids considered in the correlation step, 70% of the data present $AARDT_m$ lower than 10%, while only 3% of the data presents values of $AARDT_m$ higher than 15%. In the prediction step 13 ionic liquids were considered, and in 11 cases the absolute deviation $AARDT_m$ was lower than 10%. Also, for only two cases $AARDT_m$ was

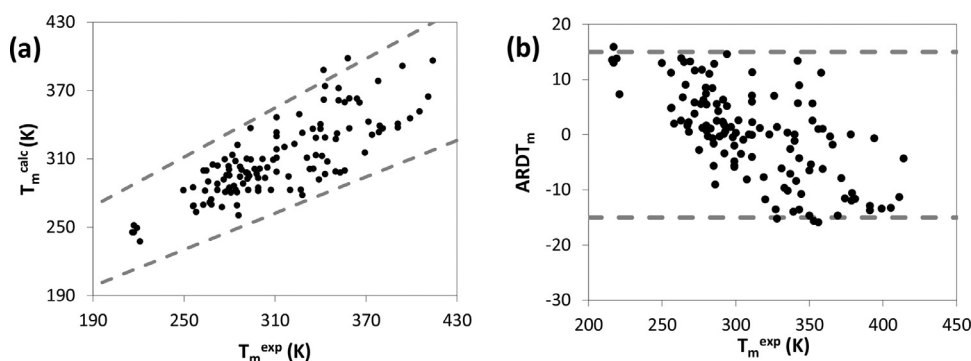


Fig. 1. A graphical picture of the correlation results: (a) experimental versus calculated melting temperature; and (b) relative deviations between experimental and calculated results. Dashed lines correspond to $\pm 15\%$ of relative deviation.

Table 4

Overall deviations of the general T_m model for the correlation and prediction steps.

Parameter	Correlation	Prediction
Number of ionic liquids	124	13
average absolute relative deviation, $AARDT_m$	6.47	6.93
maximum absolute relative deviation, $MADT_m$	15.89	16.36
average relative deviation, $ARDT_m$	0.03	4.40
maximum relative deviation: max. value of $ARDT_m$	15.89	16.36
points with $AARDT_m > 10\%$	37 out of 124	2 out of 13
points with $AARDT_m > 15\%$	4 out of 124	2 out of 13
Maximum errors (K)	57	51

Table 5

Summary of deviations for different families of cation families using the general T_m model for the correlation step.

cation	% of data points	$ARDT_m$	$AARDT_m$	$MADT_m$
imidazolium	54.03	0.64	5.86	15.63
ammonium	13.71	-3.61	6.52	15.89
pyrrolidinium	3.23	4.38	4.52	11.75
pyridinium	8.87	1.38	6.53	13.29
triazolium	12.10	0.23	10.17	15.89
phosphonium	4.84	-5.24	6.08	11.99
sulfonium	1.61	3.69	3.69	4.84
piperidinium	0.81	-1.63	1.63	1.63
tetrazolium	0.81	11.22	11.22	11.22

higher than 10%. Also, similar maximum errors below 57 K (last row of Table 4) are obtained during correlation and prediction. This value is lower than those published in the literature in which multiparametric models are used (Keshavarz et al., 2018, Venkatraman et al., 2018, Cerecedo-Cordoba et al., 2020).

More detailed results are presented in Table 5 which shows deviations between correlated and experimental values of the melting temperature for cation-families of ionic liquids. The largest family is that formed by imidazolium cation (54.03% of the data), followed by ammonium (13.71% of the data).

Fig. 1 shows the comparison between experimental and calculated melting temperature and their relative deviations ($ARDT_m$). As observed in this figure the final model estimations and the experimental data are between $\pm 15\%$ of the relative deviation. Also, Fig. 2 presents the calculated values of the heat of melting. Deviations between experimental and calculated values of heat of melting are higher than those estimated for the melting temperature. The reasons for this are not clear from the results obtained, this could be ascribed to a combination of factors: the few data available, the unknown experimental errors of these few experimental values, and of course of the inaccuracy of the simple linear model proposed (Eq. 3). Other authors have obtained similar results, using more sophisticated models. Zhu et al. (Zhu et al., 2009) used quantitative structure–property relationship approach (QSPR), including six chemical descriptors to propose a correlating and predicting

model. However, deviations of 36% during training were found and too high deviations (70% to 100%) during prediction. Later, the authors (Bai et al., 2011) improved the model by including nine quantum chemistry parameters for correlating the heat of melting of different types of ILs. One correlation data set gave maximum deviations of 20% and as high as 41% in prediction.

The usefulness and goodness of the model will not be fully tested without the prediction of melting temperatures for ionic liquids not used in the fitting of the model parameters. As explained in the data selection section, data available in the Dortmund Databank (DDB) were used for the prediction step, data that were not considered in the development of the model and in determining the model parameters presented in Table 3. From the melting temperature data included in the DDB, 13 ionic liquids were not included in determining the model parameters. Thus, T_m was predicted for these 13 ionic liquids using the same model with the same values of the parameters presented in Table 3. A summary of the results is included in Table 6.

As observed in Table 6, the melting temperature prediction varies from 281.8 K to 366.2 K and the absolute relative deviations vary from 0.7% to 16.4% (average of 6.9%). On the other hand, the enthalpy of melting (ΔH_m) is estimated with AARD of 15.9% (with maximum deviation $MAD\Delta H_m$ of 34.7%) as seen in the Supplementary Material that accompanies this paper. These values of deviations are within the errors commonly obtained for these properties (Zhu et al., 2009, Keshavarz et al., 2016, Bai et al., 2011). It is important to note that the enthalpy of melting is being directly determined by group contribution without the use of any additional physical property, as usually done by other authors (Zhu et al., 2009). Figure 3 shows the comparison between experimental and calculated melting temperatures and their relative deviations during the prediction step. Similar to the correlation step, the final model and the experimental data are, for most cases, between $\pm 15\%$ of the relative deviation.

In addition to these tests, we have also found results on melting temperature calculations presented in the literature during the latest years, so it seems to be appropriate to summarize these results and compare them with the present proposal. In Table 7, the fifth column designated as “ n_p ” indicates the number of adjustable parameters of the model, while the sixth column designated as “ n_s ” indicates the number of ionic liquids considered by the authors to propose the model. Also, NA means not applicable. On the other hand, column 7 gives the errors and deviations of different proposed models, while the last column 8 summarizes some concepts from the authors of the models.

Analyzing the information presented in Table 7, there are several observations that can be commented: (i) in almost all cases it is not clear how the available data was treated, screened and selected for correlation; (ii) some authors do not report the maximum values of deviations (models 2, 3, and 8), (iii) in most cases it is not clear what were the ionic liquids used in the correlation, testing and prediction steps (all models); (iv) some models have limited application since some few specific types of ionic liquids were considered in developing the models (model 4, 7, 8 and 10), (v) some models give unacceptable high values of deviations

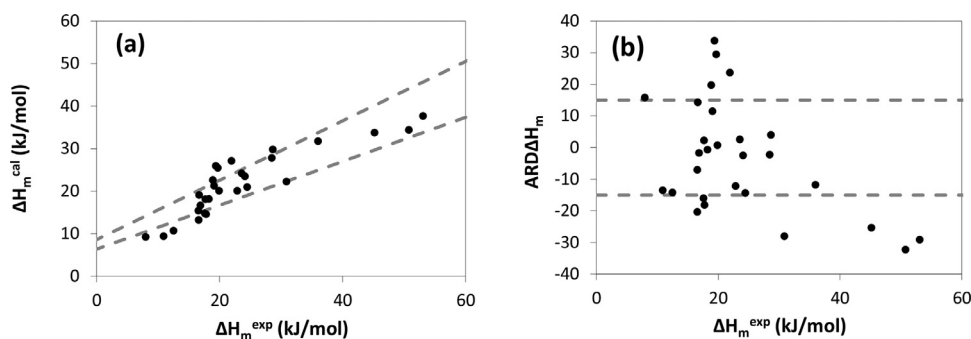


Fig. 2. A graphical picture of the correlation results for the heat of melting: (a) experimental versus calculated values; and (b) relative deviations between experimental and calculated results. Dashed lines correspond to $\pm 15\%$ of relative deviation.

Table 6

Detailed results for melting properties for the 13 ionic liquids included in the prediction step.

N°	ionic liquid	M _c (g/mol)	M _a (g/mol)	ΔH _m ^{cal} (kJ/mol)	ΔS _m ^{cal} (kJ/molK)	T _m ^{exp} (K)	T _m ^{calc} (K)	ARDT _m	AARDT _m
1	[(C4Om)2Im] [BF ₄]	241.4	86.8	23.695	0.082	281.4	289.7	2.94	2.94
2	[(C10Om)2Im] [bti]	409.7	280.2	43.249	0.151	303.1	285.7	-5.75	5.75
3	[deim] [bti]	125.2	280.2	22.943	0.081	262.6	281.8	7.30	7.30
4	[(C6Om)2Im] [BF ₄]	297.5	86.8	27.618	0.096	309.5	288.9	-6.66	6.66
5	[(C6Om)2Im] [bti]	297.5	280.2	35.402	0.124	273.8	286.0	4.44	4.44
6	[(C8Om)2im] [bti]	353.6	280.2	39.326	0.138	287.7	285.8	-0.66	0.66
7	[C4mim] [bti]	139.2	280.2	23.924	0.085	268.5	281.9	4.98	4.98
8	[C4mim] [tos]	139.2	171.2	22.015	0.069	330.2	319.1	-3.34	3.34
9	[C4mim] [ta]	139.2	113.0	19.310	0.061	296.4	319.2	7.68	7.68
10	[c2im] [TfO]	97.1	149.1	17.501	0.055	291.2	315.9	8.49	8.49
11	[C8mim] [BF ₄]	195.3	86.8	20.063	0.070	245.8	284.7	15.83	15.83
12	[P1M2,3im] [bti]	139.2	280.2	25.495	0.085	284.4	300.4	5.61	5.61
13	[C3mim] [Br]	125.2	79.9	19.123	0.052	314.7	366.2	16.36	16.36

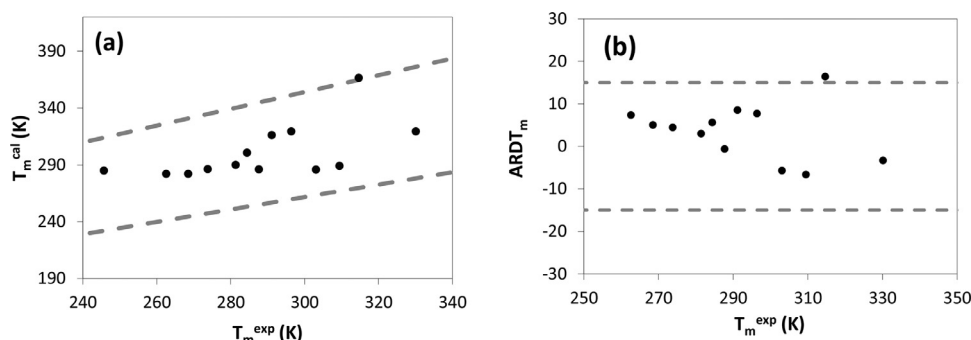


Fig. 3. A graphical picture of the predicting capabilities of the model: (a) experimental versus calculated melting temperature; and (b) relative deviations between experimental and calculated results. Dashed lines correspond to $\pm 15\%$ of relative deviation.

with respect to experimental data (models 2, 3, and 8); (vi) some models use too many adjustable parameters (models 6, and 7); and (vii) some models were developed using a few data and others do not do the testing or prediction steps (models 1, 2 and 10).

The simple model proposed in this work has similar limitations as other models presented in Table 7 with some important differences: the new model (last row in Table 7), contains fewer parameters, the calculation method can be structured in a simple and easy-to-use form through a spreadsheet provided as part of this paper, the predictive capabilities of the model have been truly evaluated, and the ionic liquids used in correlation and prediction are clearly identified.

We believe, however, that more important than the numbers obtained in this work and in the models presented in the literature during the last few years is that there is a long way to travel until we can get more general and accurate models. Still, the accuracy of the experimental data is an important issue, and the understanding of the phase change phenomenon is not clear yet. It is known that the phenomenon involves many variables that it would be difficult to measure and complex to consider in a manageable mathematical model. Despite all these difficulties, we have to recognize that all contributions that report the true findings and show veracious results, that establish the limitations of the model, and that clearly establish the capabilities of the model, will represent useful information and will contribute to the final goal of

finding the most appropriate model to estimate the melting temperature of ionic liquids for some specific applications. Most probably the general model we are all trying to find does not exist, but we can certainly make progress if more data, in quantity and quality, are available, and we can identify the most important factors that affect phase transition and the value of the melting temperature.

We should close these comments by stating that the difficulties we face today for more accurately estimating the melting temperature of ionic liquids lie in our inability to incorporate the true factors that affect the phase transition phenomenon occurring when the liquid phase goes to solid or vice versa, inability that is a consequence of our insufficient knowledge of what are those factors.

5. Melting temperature for new ionic liquids

Certainly, the most important aspect of an estimation method is the reliable calculation of the properties for other substances not considered in developing the model. In this case the melting properties of ionic liquids may be needed to be directly used in process calculations or for the estimation of other properties (Mousazadeh and Faramarzi, 2011, Atashrouz et al., 2015, Vijayraghavan et al., 2013, Lozano-Martín et al., 2020). For predicting the melting temperature of a new ionic liquids, the procedure is explained using an example, as explained in the Excel

Table 7

Selected applications for correlating and estimating the normal melting temperature of ILs showing maximum errors for each method.

N°	Author(s)	Type of ILs	Method	n _p	n _s	Errors and deviations	Comments by authors
1	(Mehrkes and Karunanithi, 2016)	imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, phosphonium-, piperidinium-	Quantum Chemistry	6	54	AARDT _m : 3.48% for correlation and 2.77% for testing. Maximum absolute deviation of 9.87% (32K). No prediction was done	The model uses several QC descriptors of the cation and anion. The authors do not indicate whose substances are used in correlation, testing and prediction steps.
2	Quill et al. (2021)	ammonium, imidazolium, morpholinium, sulphonium, phosphonium, piperidinium, pyridinium, pyrrolidinium,	Neural-fingerprinting architecture	NA	NA	Correlation: coefficient of determination is around 0.64. Max error is 240 K, and MADT _m of 40%. No-testing and prediction procedures were done.	The model uses chemical structure of the anion and cation, but the final model did not have adequate performance due to errors in estimating the molecular fingerprints.
3	(Das et al., 2017)	ammonium, pyridinium, benzimidazolium and imidazolium bromides	QSPR techniques	11	376	R ² for correlation and testing are similar and around 0.61. The maximum error is 186 K (36%). No-prediction was done.	Five models with different molecular descriptors with similar R ² of around 0.61. No information about which substances are used in correlation and testing steps.
4	(Chen and Bryantsev, 2017)	Cations: imidazolium, pyrrolidinium, and halide or polyatomic fluoro anions	Density Functional Theory	NA	11	Absolute relative deviation of correlation is 8.47%. Error in testing 54 K (11.7%). No prediction was done.	The model used lattice-free energies and ion solvation free energies. It also evaluates the stability of ILs in the crystalline and molten states using density functional theory.
5	(Keshavarz et al., 2018)	imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, phosphonium, piperidinium	Multiple linear regression method	77	243	AARD of 6.5% for correlation, 7.5% for testing. Max. error in correlation was 91 K (43.11%). No-prediction was done	The number of C, H and N atoms for cation and the number of H, N, Br, Cl, and Al atoms for the anion were used
6	(Venkatraman et al., 2018)	imidazolium-, pyridinium-, pyrrolidinium-, ammonium-, phosphonium-, piperidinium	Machine learning framework	104	NA	R ² for correlation and testing is 0.67. Errors observed are greater than 100 K in some cases. No-prediction was done.	50 molecular descriptors were used: 25 for the anions and 25 for the cations. The models analyzed in the testing step provide marginal improvements.
7	(Cerecedo-Cordoba J.J. González Barbosa et al., 2019)	imidazolium	QSPR techniques	200	415	Two data sets were studied. AARDT _m for correlation is 1.43% and 5.09%; for testing 6.43% and 3.92%. No-prediction was done.	The model includes 40 molecular descriptors. The authors used two data sets and used two different algorithms
8	(Cerecedo-Cordoba et al., 2020)	imidazolium	Neuroevolutionary trained ANN	NA	155	AARD in correlation is 5.72% and 8.41% in testing. No-prediction was done. MADT _m in correlation is 170 K (56.67%) and Testing 100 K (27.78%)	The paper is more concerned with the software rather than with calculating T _m of ionic liquids
9	(Chen et al., 2019)	Imidazolium, pyrrolidinium, pyridinium, piperidinium, tetramethylammonium, tetramethyl phosphonium,	Group contribution method	22	225	Average absolute relative deviation (AARDT _m): Correlation: 4.70% AARD; Testing: 7.09% AARD; No-prediction was done. 84 K (20.30%)	Empirical model depends on cations, anions, and substituents. The authors do not indicate which substances are used in the correlation and testing steps.
10	(Karu et al., 2019)	Choline bis[(trifluoromethyl) sulfonyl]imide	Molecular dynamics QSAR models	NA	15	Root-mean-square error is below 24 K during the correlation step. Maximum error is 43 K. No-testing and prediction have done.	Only 15 ionic liquids (having choline cations) were considered. Maximum and absolute deviations are not given
	This work	Imidazolium, ammonium, pyridinium, phosphonium, sulfonium, piperidinium, pyrrolidinium, triazolium	Semi-empirical correlation and group contribution	51	137	AARDT _m is 6.47% for correlation, 6.93% for prediction. Max error is 57 K in correlation 15.89% and 51 K in prediction (16.36%)	The model is simpler than those proposed in the literature and depends on anion and cation contributions.

file given as a supplementary material (GCM_MeltingTemp.xlsx). The instructions included in the sheet named *T_m for new ILs* must be followed.

6. Conclusions

According to the results obtained in this study, the following main conclusions can be drawn: 1) a theoretically sound group contribution model for estimating melting properties of ionic liquids has been developed; 2) the model, which is based on the well-known relation between

the melting temperature, the heat of melting, and the entropy of melting, considers different contributions for a group, depending whether the group is present in the anion or in the cation; 3) the main limitations of the model are related to the availability of the groups and the value of their contribution; 4) from the analysis of the literature and our own results it can be said that no matter how sophisticated is a model, with the present available data and with the limited knowledge of the melting process of ionic liquids, more general and accurate models cannot be developed yet.

Appendix A. Supplementary data

A spreadsheet named *JILs_GCM_MeltingTemp_2021.xlsx* for estimating the melting temperature of any other ionic liquid for which the groups are available in the MS Excel file is provided as supplementary material. In this way any result presented in this paper can be checked and the properties for any other ionic liquid can be estimated. The MS Excel file is easy-to-use and details about its functioning are provided in the MS Excel file itself. This material is available free of charge at <https://doi.org/10.1016/j.jil.2021.100002>.

Declaration of Competing Interest

There is no conflict of interest.

CRediT authorship contribution statement

José O. Valderrama: Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. **Luis F. Cardona:** Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jil.2021.100002](https://doi.org/10.1016/j.jil.2021.100002).

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