Theoretical investigation using DFT for predicting the factors affecting the melting point of series of alkylammoniumformates ionic liquids

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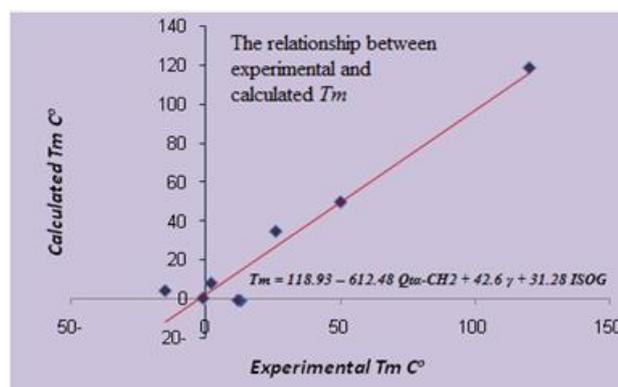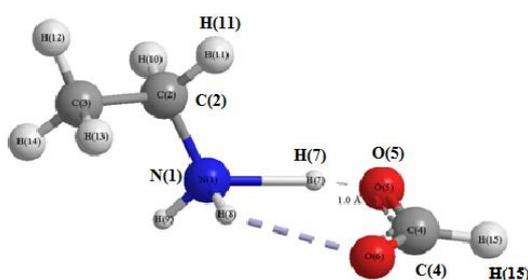*E-mail: rakhalil64@yahoo.com*

- ## Novelty and Highlights:

  1 –The introduced model of one theoretically calculated descriptor is quite helpful for interpreting the factors affecting T_m and for predicting new IL.

  2 –The use of natural population analysis (NPA) method for theoretical computational is quite significant than that of Mulliken.

- ## Graphical Abstract:

DFT model is introduced for predicting the factors affecting the melting point of series of alkylammoniumformates ionic liquids.

Theoretical investigation using DFT for predicting the factors affecting the melting point of series of alkylammoniumformates ionic liquids

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Abstract: The synthesis of new salts of ionic liquids (ILs) is still within the term of trial and error in spite of their pronounced importance in many essential aspects. Consequently, quantum mechanical calculations based on density functional theory (DFT) have been performed for understanding the factors affecting the melting point (T_m) for series of nine alkylammoniumformates ILs. It has been found that the molecular charge distribution of ILs plays a major role in determining the T_m of these ILs. A model of one-descriptor representing the charge including two correction terms with sufficient statistical parameters (correlation coefficient and standard deviation equal to 0.967 and 13.6^{o}C respectively) has been introduced. It has been found that the computational method of natural population analysis (NPA) is the more appropriate for molecular charge estimation as not needing big basis set in contrast to that of Mulliken method.

Keywords: ionic liquids; alkylammoniumformate; density functional theory; computational chemistry; Mulliken charge; natural population analysis.

Introduction

Ionic liquids (ILs) are considered to be as new generation of green chemistry in contrast with that of relative popular organic solvents. In fact, the employment of these condensed salts is not limited for environmental aspects. It extends to further advantages resulting from their unique characterized properties that work as controller and designer solvents. These properties are behind huge chemical, biological and industrial applications of such interesting molecules. However, the theoretical bases for the pronounced physical properties of ILs are considerably still not clear. Therefore, investigation concerning such aspect must take more attention by the scientists who specified in this field. According to literature, there are considerable numbers of articles dealing with combination of melting points of ILs with theoretical parameters have been noticed [1-25]. Most of these studies were captured by quantitative structure property relationship (QSPR) [1-7, 11, 14-19, 23]. Although, few studies were carried out using group contribution method (GCM) for such purpose [20-22]. In fact, the first model for predicting the melting point of ILs was introduced at 2002 by Katritzky and his coworkers [1]. Afterward, many of models for different classes of ILs were developed in order to be as helpful tool for synthesizing new types of ILs [2-25].

In general, all of these investigations have been focused upon the employing of the theoretical calculations for prediction the melting point (T_m) of ILs. Indeed, such studies are quite interest which could give indication for predicting new ionic liquids. However, the suggested models of prediction T_m were based on statistical analysis aspects. Therefore, one should expect that the descriptors of these models are not reflecting the physical factors affecting the melting point. This can be attributed to the fact that the statistical treatment for such purpose is not an exact method in contrast to that of mathematical [26]. In other words, statistical method is adjusted in such a way in order to give the best values of correlation coefficient (r) and standard deviation (SD). Furthermore, attention must be taken by researchers who dealing with statistics from the numbers of both observations and descriptors points of views. For example, the values of r and SD are significantly improved by increasing either the number of observations or descriptors.

Several studies supposed that ILs ions may packed regularly (pseudo-crystalline) which based on stacking of mutual charges or ordered association of cation species with related cation-anion interactions and vice versa [27-29]. The models proposed by Lopes et al. [30] suggested that the resulted dynamic nano-domained structure of ILs arises from the head groups that bearing the ionic charges. In other words, the polar charges in the head groups are the main

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reason for the aggregation between ion pair and then will be the controller of T_m through influencing the crystal packing ability of the ionic liquid. Indeed, the presence of permanent charges in ILs structures in contrast to that of temporary dipoles in conventional molecular solvents causes what is called as "ionic liquid effect". Efforts have also been made by scientists in order to correlate T_m of ILs with interaction energy [24-25].

In this work, an attempt has been presented for developing a model having a physical meaning for alkylammoniumformate ILs that could be helpful tool for predicting their T_m and understanding the main factors affecting the melting points of these salts. In addition, we have employed density functional theory (DFT) for theoretical calculations, which only few literatures [24-25] have been observed for using this method in this field in contrast to the related other published researches [8-10,12-13]. It should be noted that quantum mechanics computations based on DFT can be considered as a powerful tool for solving chemist and chemistry problems [31,32].

Nomenclature

AM	ammonium
BuAM	butylammonium
C	Coulomb unit
DFT	density functional theory
ΔQtP	net difference between polar groups
EAM	ethylammonium
γ	gamma effect
GCM	group contribution method
ILs	ionic liquids
ISOG	isopropyl group effect
MAM	methylammonium
2MBuAM	2-methylbutylammonium
3MBuAM	3-methylbutylammonium
MM2	molecular mechanics
2MPrAM	2-methylpropylammonium
NPA	natural population analysis
PeAM	pentylammonium
PM3	Parameterized Model number 3
PrAM	propylammonium
$Q\alpha\text{-}CH_2$	charge of alpha carbon
QN	charge on N atom of cation head group
QSPR	quantitative structure property relationship
QtA	total charge of anion
QTail	total charges on the hydrocarbonic tail
QtHGC	total charge on polar head group of cation
Qtn-CH2	total charge on hydrocarbonic groups
r	correlation coefficient
SD	standard deviation
T_m	melting point

Experimental (Computational Methodology)

Quantum chemical calculations that based on DFT were used for all the presented computations. These were performed using Gaussian 03W program [33] that is working within ChemBioOffice 2008 package. Optimized structure and energy of the most stable conformer of the ionic pairs was further minimized using the hybrid DFT method (DFT/B3LYP), together with the basis set of 6-31++G(d,p).

The T_m values of nine alkylammoniumformates ILs including, ammonium (AM), methylammonium (MAM), ethylammonium (EAM), propylammonium (PrAM), butylammonium (BuAM), pentylammonium (PeAM), 2-methylpropylammonium (2MPrAM), 2-methylbutylammonium (2MBuAM) and 3-methylbutylammonium (3MBuAM) were taken from Reference 34.

In order to reach the optimum conformer for the ion pairs as having excellent geometry with less energy, a placement of the anion in four locations around the cation (top, bottom, left and right). Then, the favorable geometry for atoms and bonds in ionic liquids was obtained using molecular mechanics (MM2). Afterward, the optimizations have been completed for those four conformers through employing semi-empirical method of Parameterized Model number 3 (PM3). Hence, the optimum conformer of the least energy has been considered as the true sample that representing the ionic liquids for calculation. The next step was carried out using DFT based on B3LYP with 6-31++G(d,p) basis set theoretical level as an additional optimization for the electronic structure and geometry. A similar procedure was used for estimation the charges distribution by both Mulliken and natural population analysis. It should be noted that the calculations on the ethylammoniumformate (EAM) using fifteen basis sets showed that the addition of diffuse and polarize functions to double-zeta basis sets for both the heavy and light atoms will reduces the ground state energy. Therefore, the basis set of 6-31++G (d, p) is considered as the most appropriate choice from the fifteen of used basis set in this investigation. Indeed, the ethylammoniumformate can be used as a sample that representing the alkylammoniumformates of which they employed in this study due to the apparent similarity in their molecular structures. Therefore, the effect of basis set type on the calculated value of charge distribution has been investigated for EAM (Figure 1) as an example through using both Mulliken and natural population analysis (NPA) methods. Such study could be

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considered as a helpful way for selecting the suitable method for such purpose. In other words, the method that gives fewer differences between calculated values of different basis set might be considered as more favorable from the accuracy and time consuming points of views. Interestingly, the results of such estimation (Table 1) indicate according to the corresponding standard deviation values that the NPA method is much better than that of Mulliken. Therefore, we could do this job simply using small basis set in contrast to that of relatively much time consuming (middle and big basis sets) for calculations the charge distribution using NPA method only. Whatever, a basis set of 6-31++G(d,p) has been selected for the presented study as giving the lower ground state energy in comparison with other smaller basis sets as shown clearly in the Table 1. Finally, Minitab software (release 14.1) was performed for statistical analysis (simple and multiple regressions).

Table 1 Comparing the charges values in Coulomb unit of selected atoms (Figure 1) in ethylammoniumformate that calculated by Mulliken and NPA methods based on DFT / B3LYP with 15 basis sets.

	Charge (Coulomb) X1000 Mulliken (NPA)						
Basis set	N(1)	C(2)	C(4)	O(5)	H(7)	H(11)	H(15)
3-21G	-726[a] (-883)[b]	-241 (-273)	404 (520)	-579 (-664)	389 (445)	224 (244)	178 (155)
3-21G*	-726 (-885)	-241 (-274)	404 (526)	-579 (-667)	389 (462)	224 (240)	178 (158)
3-21G**	-520 (-886)	-124 (-277)	483 (527)	-499 (-666)	303 (463)	152 (239)	119 (158)
3-21+G*	-835 (-931)	-445 (-302)	270 (592)	-485 (-739)	513 (500)	290 (249)	218 (164)
3-21+G**	-535 (-911)	-335 (-304)	352 (586)	-399 (-751)	420 (490)	199 (255)	154 (158)
6-31G	-773 (-916)	-116 (-283)	342 (570)	-572 (-743)	446 (502)	166 (250)	138 (163)
6-31G(d)	-769 (-923)	-0.132 (-261)	361 (646)	-564 (-727)	456 (506)	161 (233)	124 (140)
6-31G(d,p)	-0649 (-925)	-057 (-268)	419 (640)	-488 (-738)	371 (509)	122 (238)	085 (140)
6-31+G	-1.036 (-937)	-171 (-310)	281 (567)	-499 (-748)	545 (510)	218 (255)	167 (171)
6-31++G	-972 (-917)	-318 (-285)	214 (578)	-458 (-723)	570 (511)	230 (237)	174 (161)
6-31+G(d)	-1018 (-941)	-186 (-287)	304 (643)	-0.562 (-736)	579 (516)	209 (237)	158 (146)
6-31+G(d,p)	-786 (-944)	-132 (-293)	346 (639)	-456 (-747)	471 (519)	155 (242)	112 (147)
6-31++G(d)	-987 (-910)	-283 (-262)	230 (646)	-538 (-735)	609 (510)	226 (227)	174 (139)
6-31++G(d,p)	-745 (-917)	-206 (-267)	283 (644)	-431 (-074)	506 (512)	165 (229)	113 (141)
Standard deviation (SD)	0.165 (0.020)	0.105 (0.016)	0.076 (0.049)	0.059 (0.032)	0.089 (0.023)	0.044 (0.009)	0.036 (0.011)

[a]UsingMulliken method; [b]using NPAmethods

Results and discussion

Table 2 lists the calculated physical properties using DFT for the presented series of ILs. These properties are include total charge on polar head group of cation ($-NH_3^+$) which symbolized as QtHGC, total charge of anion (QtA), charge on the nitrogen atom of cation head group (QN), charge of alpha carbon including related hydrogen atoms ($Q\alpha$-CH_2), total charge on all non-polar hydrocarbonic groups beyond head group (Qtn-CH2) including related hydrogen atoms, and total charges on the hydrocarbonic tail (QTail).
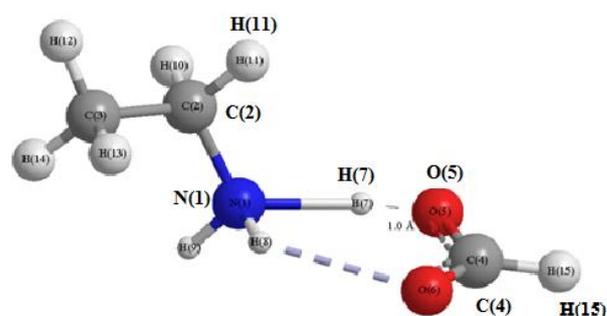

Figure 1 Shows the optimized molecular structure of EAM formate using DFT (B3LYP) 6-31++G (d, p) method.

As far as the presented ILs containing fixed anion (formate), the net differences between total polar positive charge and total polar negative charge in ion pair (ΔQtP) was suggested in order to include the effect of anion as represented in Figure 2 and the following equation:

$$\Delta QtP = (q^+ - q^-)_{polar} \quad (1)$$

where q^+ is the total of positive charges on hydrogen and carbon atoms at polar region only and q^- is the total of negative charges on nitrogen and two oxygen atoms at polar region only, as clearly illustrated in Figure 2. Such a parameter may represent the charges consumed by ion pair of ionic liquid. Then, the remaining charge would be responsible for packing the pairs of ionic liquid through molecular interactions and therefore increases the melting point.
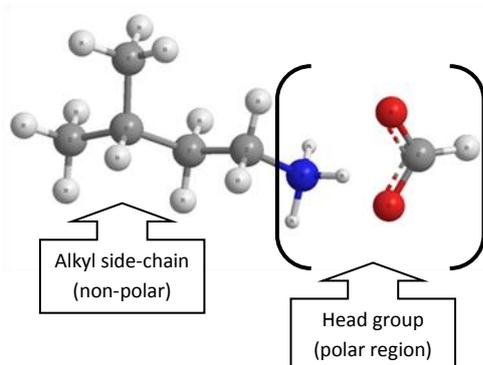
Figure 2 Explain polar and non-polar regions in 3-methylbutylammonium formate (3MBuAM) as example for alkylammoniumformate.

Table 2 Theoretical calculated charges in Coulomb unit (C) of a series of alkylammoniumformates ILs using DFT (B3LYP) 6-31++G (d, p) method.

ILs	T_m* C°	QtHGC	QtA	QN	Qα-CH2	Qtn-CH2	ΔQtP	Qtail
				Charge (Coulomb)				
AM	120	0.598	-0.598	-1.141	0.000	0.000	5.054	0.000
MAM	13	0.41	-0.606	-0.924	0.195	0.195	4.433	0.195
EAM	-15	0.413	-0.607	-0.918	0.187	0.194	4.424	0.007
PrAM	50	0.409	-0.605	-0.92	0.182	0.196	4.419	0.022
BuAM	2	0.414	-0.607	-0.918	0.181	0.192	4.424	0.021
PeNAM	12	0.417	-0.607	-0.914	0.195	0.190	4.42	0.017
2MPrAM	26	0.411	-0.602	-0.922	0.188	0.191	4.428	0.060
2MBuAM	-1	0.412	-0.603	-0.924	0.193	0.192	4.435	0.045
3MBuAM	47	0.416	-0.607	-0.918	0.183	0.191	4.427	0.053

*Taken from Ref. 34.

Indeed, a general correlation matrix is quite necessary for finding the best relationship between the calculated values of physical properties with their practical values of T_m as illustrated in Table 3. Such a matrix will be quite helpful in order to verify if there is any correlation between the estimated properties with each other. The values of correlation coefficient (Table 3) indicating there is a good relation between all suggested parameters with the T_m except for that of QTail. In turn, the values of r that listed in Table 3 suggesting that the most of these parameters are depending on each other and that the charges distribution plays a major role on the T_m of the presented ILs. Thus, the parameter of charge of alpha carbon including related hydrogen atoms ($Q\alpha$-CH_2) was selected in order to build up the suggested model as relatively possessing the best value of r (Eq. 2):

$$T_m = 121.16 - 555.9 \, Qt\alpha\text{-}CH_2 \qquad (2)$$

Table 3 Pearson correlation coefficient (*r*) resulted from the correlation matrix that representing the relationship

between the calculated charges of alkylammoniumformate ILs with the experimental values of T_m [34].

Descriptor	T_m [34]	ΔQtP	QN	QtHGC	Qtα-CH2	Qtn-CH2	QtA
ΔQtP	0.845						
QN	-0.849	-1.000					
QtHGC	0.844	0.999	-0.997				
Qtα-CH2	-0.863	-0.995	0.994	-0.995			
Qtn-CH2	-0.846	-0.999	0.998	-1.000	0.995		
QtA	0.701	0.813	-0.823	0.790	-0.792	-0.807	
QTail	-0.213	-0.280	0.270	-0.309	0.335	0.305	-0.158

It should be noted that the intercept of this model represents the approximate value of T_m for ammonium formate (120°C) which there is no α-CH_2 group in its structure. At the same time, this gives a significant support for this model from statistical point of view as containing only one descriptor with r and SD equal to -0.863 and 21.9°C respectively.

In general, the inverse dependency of T_m on α-CH_2 with inverse proportionality can be explained in terms of the presence of α-CH_2 group which could reduce the value of the positive charge on the head group of cation (NH_3^+). This due to that the methyl group is considered as a donating group of electrons as realized from the values of charges on the head group (NH_3^+) that listed in Table 2. In other words, the highest value of the charge that located on the head group of ammonium formate is 0.598C (Coulomb unit) which not containing methyl group, but when linked with last group the charge was decreased to about 0.41C. Hence, the reduction in the amount of positive charge on the polar head group due to presence of α-CH_2 makes a weakness in the strength of the electrostatic interaction with the anion and thus decreasing the T_m.

The fitted values of T_m using model 2 that listed in Table 4 give an indication for a secondary effect which can be named as gamma effect (γ) that only present in one IL (PrAM). Such an effect is resulted from the presence methyl group (-CH_3) in gamma position which could make some effect on the ammonium group of cation from stereo-chemical point of view (Figure 3). Thus, a corrective parameter (γ) having values of 1 for PrAM and zero for others may be added to Eq. 2. The results of multiple linear regressions show a remarkable improvement from statistical point of view (r=0.906 and

SD= 19.7^{o}C) due to presence of this parameter as can be presented by this model:

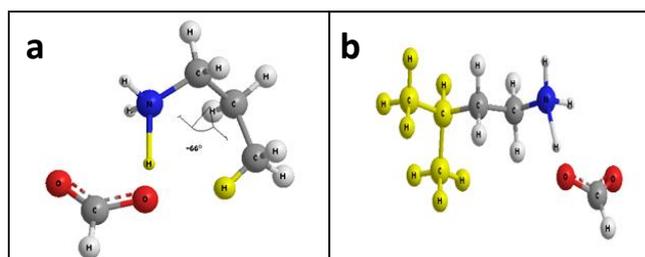$$T_m = 120.06 - 572\ Qt\alpha\text{-}CH_2 + 34.1\ \gamma \quad (3)$$

Figure 3 Illustrates in yellow color (a) gamma effect, γ and (b) the presence of isopropyl group, ISOG.

Indeed, the γ effect can be realized from the measurements of dihedral angle which having values of -66° for PrAM except than that of the presence of an isopropyl group. In other words, there is what so called gauche interaction when -CH_3 group in gauche position with ammonium ion as their dihedral angle is close to 60°. On the other side, the dihedral angle of the rest of other ions pairs are between 171° and 180° which have no γ interaction as they in eclipsed or anti conformation [35]. Another factor may be recognized from the differences between experimental and fitted values (Table 4) is due to the presence of isopropyl group which only exists in two ILs (2MPrAM and 3MBAM). This factor was symbolized as *ISOG* which also could be considered as a correction term and have values of one for IL possesses isopropyl group (2MPrAM and 3MBuAM) and zero for others as shown in Figure 3. The results of multi-linear regression also give remarkable improvement in Eq. 2 from statistical point of view due to the addition of this correction term as represented by the following model (r =0.902 and SD=20.23^{o}C).

$$T_m = 120.49 - 584.6\ NB\ Qt\alpha\text{-}CH2 + 24.53 ISOG \quad (4)$$

It is clearly shown from the last equation as the sign of the correction factor (ISOG) is positive which causing an increase in T_m. On the other hand, it is well known that the presence of isopropyl group reduces the dispersion forces between hydrophobic groups in contrast to that of linear chain. Such contradiction may be attributed to that the presence of such a bulky isopropyl group makes the arrangement of ILs molecules in opposite direction which therefore eliminates the dispersion forces and at the same time increase the electrostatic forces between polar groups.

The significant improving of the last two models due to presence of the correction terms may suggest for gathering both of these terms in one model as presented in equation 5. The statistical parameters also enhanced considerably which having values of 0.967 and 13.6^{o}C for r and SD respectively.

$$T_m = 118.93 - 612.48\ Qt\alpha\text{-}CH2 + 42.6\ \gamma + 31.28\ ISOG (5)$$

Table 4 Shows fitted values of the theoretically calculated T_m from suggested models.

IL	T_m^{o}C [34] Experimental	Model 1 (Eq. 2) ^{o}C	Model 2 (Eq. 3) ^{o}C	Model 3 (Eq. 4) ^{o}C	Model 4 (Eq. 5) ^{o}C
AMN	120	121.16	120.06	120.49	118.93
MAM	13.0	12.52	8.28	6.26	-0.76
EAM	-15.0	17.22	13.12	11.20	4.42
PrAM	50.0	19.93	50.00	14.05	50.00
BuAM	2.00	20.76	16.76	14.93	8.32
PeNAM	12.0	12.78	8.54	6.53	-0.48
2MPrAM	26.0	16.50	12.37	34.98	34.90
2MBuAM	-1.00	13.73	9.52	7.53	0.57
3MBuAM	47.0	19.40	15.35	38.02	38.10

Interestingly, these models do not show remarkable change in the weight of their coefficients including the constant term (intercept) which strongly support their physical significant. In other words, the effect of charge distribution is the main factor that affecting T_m of ILs due to relatively very high weight (612.48) of its coefficient in contrast to that of others (42.6 and 31.28 for γ and *ISOG* respectively). In turns, the ΔQtP parameter which represents the net difference between the polar groups of negative and positive charges have a considerable proportionality with T_m (r= 0.845) as presented clearly in Table 3. At the same time, this parameter (ΔQtP) has a perfect inverse proportionality (r=-0.995) with $Qt\alpha\text{-}CH2$ which by substituting it in T_m would mostly be depend on the strength of charge distribution. For instance, substitution of $Qt\alpha\text{-}CH2$ in Eq. 5 by (ΔQtP) gives an excellent relation (6) with r equal to 0.972 and SD equal to 12.17^{o}C. Equation 6 show clearly that the T_m of ILs increases with increasing ΔQtP parameter which could be related to intermolecular interactions. At the same time, the amounts and signs of the coefficients of corrective terms for this model are quite parallel and close to those of model 5 which also give extra confident to the presented approach. Actually, the pronounced dependency of T_m on charge distribution may be related to the formate anion (organic) that makes the charge not localized on one atom in contrast to that of halogen anion [36]. Indeed, the relatively high value of correlation coefficient (r= 0.967) expresses the efficiency of the suggested model (5) for predicting the melting point of ILs based on formate anion. This can be attributed to that

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during the melting point process there is dissociation in the non-fixed bonds (nonionic and non-covalent) such as ion-dipole, ion-induced dipole, and dipole-dipole and so on. Therefore, such intermolecular interactions are depending on the difference between opposite polar charges which the electrostatic interactions depend on the strength of electrical charge [37]. Therefore, when increasing of the difference between highest polar positive charge and highest polar negative charge of ion pair will consequently enhances the specific interactions and thus increase the melting point. Hence, the charge distribution can be used as a reliable function for predicting melting point of ionic ILs.

$$T_m = -829.58 + 187.88 \, \Delta QtP + 49.33 \, \gamma + 34.24 \, ISOG \quad (6)$$

The correction terms that presented by γ and *ISOG* coefficients are showing bad effect on T_m which must be avoided by ILs designers as enhancing the melting point. The results of Table 2 show there is no good proportionality between the total charges on the hydrocarbonic tail of the cation (QTail) with the others. This observation could be explained in terms of that the charges on polar portion are relatively quiet greater than that on hydrophobic part. In other words, the charges on polar part are responsible for the most electrostatic interactions between molecules and therefore have a sufficient effect on T_m of ILs.

It should be noted that the use of NPA method also gives a better results from statistical point of view in contrast to that of Mulliken. For example, the relationship between T_m and $Qt\alpha\text{-}CH_2$ using Mulliken method is relatively weaker than that of NPA which have values r equal to -0.707 and -0.86 respectively. Therefore, this could add a further support for employing NPA method for such investigations by computational chemists.

According to literature, no model consisting direct combination between T_m with charge has been suggested. In addition, no theoretical investigations concerning the presented ILs (alkylammoniumformate) is found. Furthermore, a unique feature of the presented model in comparison with related published works [1-25] is that it possesses dual characteristics that gathering both of physical meaning for understanding the T_m of ILs and of statistical significant for predicting new ILs according to r value. However, the expression of charge has been used by Sun et al. [11] as partial charges of hydrogen atoms as a descriptor within three- and six-descriptors models for imidazoliumtetrafluoroborates (r=0.951) and imidazoliumhexafluorophosphates (r=0.959) ILs respectively. Trohalaki et al. [5] have employed the property of weighted surface charge of hydrogen-bond acceptor atoms as a parameter in three-descriptors for 4-amino-1,2,4-triazolium bromide and nitrate salts with r equal to 0.933. Finally, Li et al. [24] and Wei et al. [25] have used the property of interaction energy which depends on charge as a descriptor in their models for alkyl imidazoliumtetrafluoroborate and amino acid cation based ILs which gives r equals to 0.848 and 0.787 respectively. Whatever, application of the presented models for other types of ILs can be considered as a future work.

Conclusions

On the basis of the above results one could generally conclude that the charge distribution is the main factor that affecting the T_m of series of nine alkylammoniumformates ILs. A model with only one descriptor and two correction terms has been constructed which can be quite helpful for understanding the factors affecting the T_m of ILs. This model is considered to be as a sufficient tool that could aid researchers for synthesis a new ILs. The results indicate that there are three main factors could increase the T_m which must be avoided by those researchers. The first is considered as the predominant one which is resulted from the increasing in difference between highest polar positive charge and highest polar negative charge (ΔQtP). The second and third are belonging to stereochemical or geometrical aspect (γ and *ISOG* effects) as they resulted from the correction terms. In other words, the extending of charge distribution through ion decreases the T_m (good effect), then when the difference between charges of cations and anion decreased the T_m also decreased in order to be IL not as conventional salt. For example, the difference in charge is only applicable through the presence of charge distribution with presence of at least one ion of multiple atoms not for charge localized ions such as NaCl salt. Thus, if the difference between charges of cation and anion is small, therefore, the net charge remained will be not that effective for making a strong molecular interactions particularly through electrostatic forces and then reduces the packing between IL molecules.

On the other side, the computational results indicate that the use of NPA method is quite significant than that of Mulliken. This due to that the former method is relatively not affected remarkably through changing the basis set which will be less time consuming through using low basis set.

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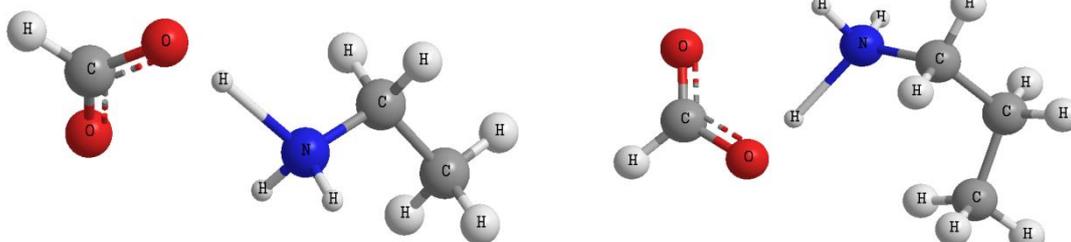37. M. Karelson, V. S. Lobanov and A. R. Katritzky, *Chem. Rev.*, 1996, **96**, 1027.

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Supplementary information

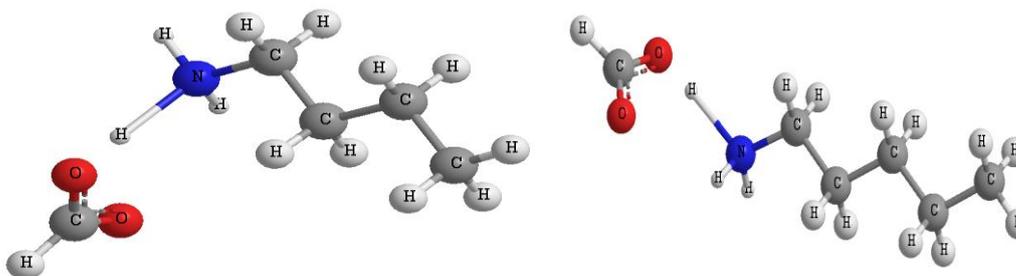Optimized chemical structures of alkylammoniumformates ionic liquids
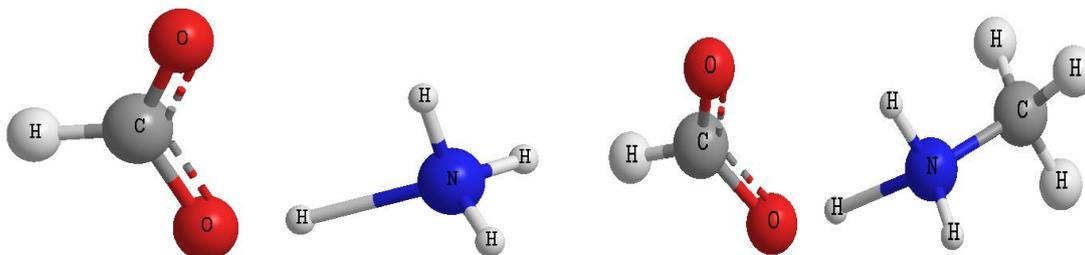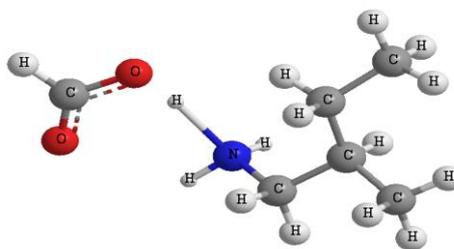

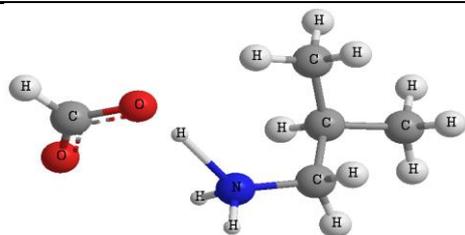| Ammonium formate | Methylammonuim formate |

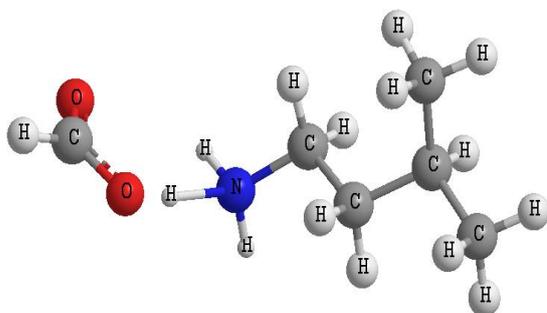| Ethylammoium formate | Propylammonium formate |

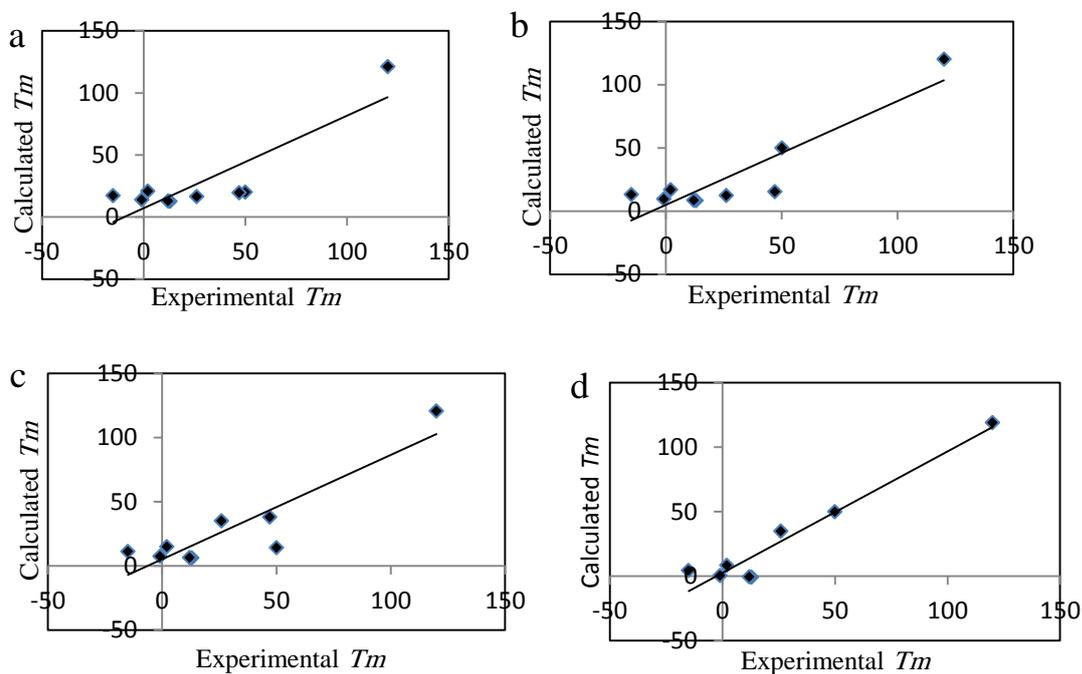| Butylammonium formate | Pentylammonium formate |

2-Methyl propylammonium formate

2-Methyl butylammonium formate

3-Methylbutylammonium formate

Relationship between experimental and calculated melting point according to: a) Eq2, b) Eq3, c) Eq4, d) Eq5.