A Novel Method for the Prediction of the Impact Sensitivity of Quaternary Ammonium-based Energetic Ionic Liquids

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Abstract: Impact sensitivity is an important safety parameter for the assessment of the hazards of working with new energetic compounds including ionic molecular energetic materials. This paper introduces two novel simple correlations to assess the impact sensitivity of quaternary ammonium-based energetic ionic liquids, which are based on the elemental composition of cations and anions divided by the molecular weight of a desired ionic liquid as well as the contribution of specific cations and anions. For 72 ionic molecular systems as a training set, the root mean square (rms) deviations of predictions for these models relative to experiment are 11 J and 6 J, respectively. The reliability of the models has also been tested for a further three ionic compounds containing complex structures, which give rms deviations of 12 J and 6 J, respectively, with respect to the measured data. The results of the current study indicate that the accuracy of this novel method for the prediction of the impact sensitivity of quaternary ammonium-based energetic ionic liquids is not necessarily enhanced by greater complexity.

Keywords: correlation, quaternary ammonium-based energetic ionic liquid, impact sensitivity, safety

1   Introduction

The environment, the cost associated with both facility clean-up and disposal of chemical waste are important problems in the synthesis and testing of an energetic material. Prediction of the performance and sensitivity of an energetic compound can provide scientists and engineers considerable insight into the understanding of factors affecting these parameters [1-4]. The sensitivity of an energetic material is a consequence of the kinetics and thermodynamics of its thermal decomposition. The impact stimulus needed depends on the ease with which a detectable reaction of any kind can be initiated in an energetic compound.

Impact sensitivity is the easiest method as it involves simply the dropping of a weight, *e.g.* a 2.5 kg mass, from a predetermined height onto a striker plate [4]. This parameter is measured by the height from which there is a 50% probability of causing an explosion. Even though there are the uncertainties associated with the impact sensitivity test, different methods have been developed for the prediction of the impact sensitivity of different classes of neutral energetic compounds, and these have been reviewed elsewhere [1, 5-11]. Since the impact sensitivity of an energetic material depends on the particle size distribution, morphology and the basic molecular structure, the results are often not reproducible [12-14]. For example, the reported values of the impact sensitivities for twice-recrystallized 2,4,6-trinitrotoluene vary from below 25 J to above 61 J [15].

In contrast to the impact sensitivity of neutral energetic compounds where there are many predictive methods, only Politzer *et al.* [16] have recently used a quantum mechanical approach to investigate qualitatively the relationship of the impact sensitivity of energetic ionic liquids with the maximum available heat of detonation, the amount of free space per molecule (or per formula unit) in the crystal lattice and specific features of the electrostatic potential on the molecular or ionic surface. The purpose of this work was to develop a novel method for the prediction of the impact sensitivity of a quaternary ammonium-based energetic ionic liquid from its molecular structure. The importance of being able to do this is that impact sensitivity is the main source of many accidents in work-places where new energetic compounds are handled. It will be shown that the new method can be applied to quaternary ammonium-based energetic ionic liquids containing complex structures for which experimental data have been reported.

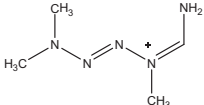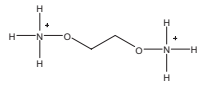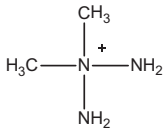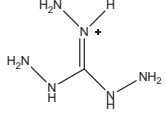# 2   Results and Discussion

2.1 Development of the new models
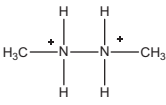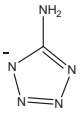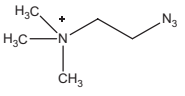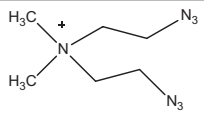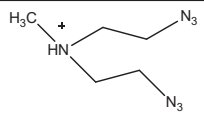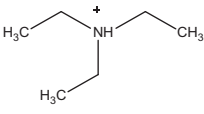
The elemental compositions of different classes of energetic compounds are important parameters for assessment of their impact sensitivities [5-10, 17-20]. For ionic liquids, it has been found that the elemental composition and the contributions of some cations or anions are important for the assessment of some properties such as density [21, 22]. Experimental data for 72 ionic molecular energetic materials with general formula CHNOCl are given in Table 1. This information has been used to correlate their elemental compositions and structures with impact sensitivity. The results have shown that the following general equation, which was obtained by the best fit to experimental impact sensitivity data through the multiple linear regression method [23], can correlate with the elemental composition of cations and anions as:
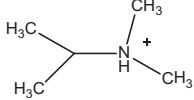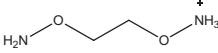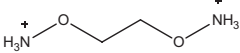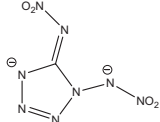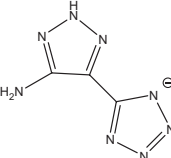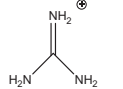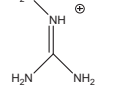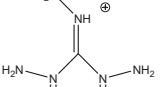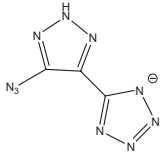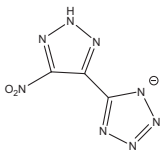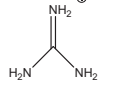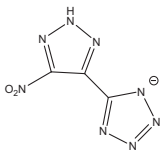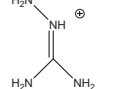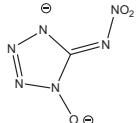
$$IS_{IL}(J) = 30.50 + \frac{-965.9(n_C)_{cat} + 756.2(n_H)_{cat} - 1653(n_O)_{cat} + 1164(n_C)_{ani} + 1135(n_H)_{ani} - 1233(n_N)_{ani} - 902.2(n_O)_{ani}}{Mw} \quad (1)$$
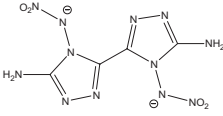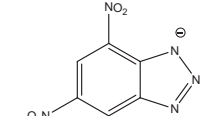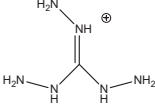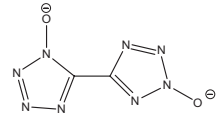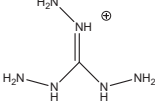
where $IS_{IL}(J)$ is the impact sensitivity of a desired energetic ionic liquid in J; $(n_C)_{cat}$, $(n_H)_{cat}$ and $(n_O)_{cat}$ are the number of carbon, hydrogen and oxygen atoms in the cation, respectively; $(n_C)_{ani}$, $(n_H)_{ani}$, $(n_N)_{ani}$ and $(n_O)_{ani}$ are the number of carbon, hydrogen, nitrogen and oxygen atoms in the anion, respectively; Mw is the molecular weight of the desired quaternary ammonium-based energetic ionic liquid. The contributions of the other elemental compositions are small, and can thus be neglected because their presence does not change the coefficient of determination or R-squared values of Equation 1. In contrast to neutral energetic compounds, the elemental compositions of cations and anions are separately important. However, the relative weights of the coefficients of the same elements such as oxygen atoms in the cations and anions are different. Furthermore, increasing $(n_O)_{cat}$ and $(n_O)_{ani}$ can decrease the value of $IS_{IL}(J)$ because these variables have negative coefficients.

Table 1. Comparison of the predicted $IS_{IL}(J)$ and $IS_{IL}^{corr}(J)$ of ionic liquids by Eqs. (1) and (2) with the experimental data

Cation	Anion	IS_{Exp} [J]	Eq. (1)	Dev	Eq. (2)	Dev
	NO_3^-	40 [29]	29	-11	28	-12
	ClO_4^-	35 [29]	31	-4	31	-4
	N_3^-	40 [29]	31	-9	30	-10
		40 [29]	36	-4	34	-6
	NO_3^-	40 [29]	35	-5	35	-5
	ClO_4^-	40 [29]	36	-4	36	-4
	N_3^-	40 [29]	37	-3	37	-3
	$N(CN)_2^-$	40 [29]	49	9	48	8
		40 [29]	33	-7	35	-5
		40 [29]	42	2	41	1
		40 [29]	41	1	40	0
	NO_3^-	50 [29]	41	-9	40	-10
	ClO_4^-	40 [29]	41	1	41	1
	$N(NO_2)_2^-$	12 [29]	20	8	20	8
		50 [29]	47	-3	45	-5
		2 [29]	23	21	0	-2
		10 [29]	19	9	19	9

Cation	Anion	IS_{Exp} [J]	Eq. (1)	Dev	Eq. (2)	Dev
(structure)	NO_3^-	30 [29]	33	3	33	3
	ClO_4^-	15 [29]	34	19	15	0
	N_3^-	30 [29]	35	5	35	5
(structure)	$N(NO_2)_2^-$	2 [29]	7	5	9	7
(structure)	Cl^-	60 [30]	56	-4	59	-1
	$(N(CN)NO_2)^-$	60 [30]	38	-22	61	1
	$N(CN)_2^-$	60 [30]	61	1	59	-1
	$C(NO_2)_2(CN)^-$	60 [30]	34	-26	51	-9
	$C(NO_2)(CN)_2^-$	60 [30]	50	-10	49	-11
	$C(CN)_3^-$	60 [30]	70	10	68	8
	NO_3^-	60 [30]	43	-17	69	9
(structure)	$N(NO_2)_2^-$	4 [31]	24	20	5	1
(structure)	NO_3^-	30 [32]	23	-7	25	-5
	$N(CN)_2^-$	40 [32]	39	-1	40	0
(structure)	*(structure)*	60 [32]	41	-19	64	4
(structure)	N_3^-	40 [32]	38	-2	37	-3
	$N(CN)_2^-$	40 [32]	49	9	47	7
	$(N(CN)NO_2)^-$	40 [32]	34	-6	33	-7
	$N(NO_2)_2^-$	40 [32]	21	-19	36	-4
(structure)	$N(CN)_2^-$	40 [32]	40	0	39	-1
	$(N(CN)NO_2)^-$	40 [32]	34	-6	34	-6
(structure)	$(N(CN)NO_2)^-$	40 [32]	30	-10	30	-10
(structure)	N_3^-	40 [32]	49	9	45	5

Cation	Anion	IS_{Exp} [J]	Eq. (1)	Dev	Eq. (2)	Dev
(diisopropyl-dimethyl ammonium structure)	N_3^-	40 [32]	46	6	43	3
(H₂N–O–CH₂CH₂–O–NH₃⁺ structure)	NO_3^-	9 [32]	15	6	14	5
	$N(NO_2)_2^-$	3 [32]	2	-1	2	-1
(H₃N⁺–O–CH₂CH₂–O–NH₃⁺ structure)	$N(NO_2)_2^-$	2 [32]	7	5	9	7
NH_4^+	(nitramino-tetrazole anion structure)	1.5 [33]	3	1	4	2
$N_2H_5^+$		1 [33]	12	11	0	-1
NH_3OH^+		1.5 [33]	-2	-4	-1	-3
NH_3OH^+	(amino-triazolyl-tetrazolate anion structure)	25 [34]	22	-3	21	-4
(guanidinium structure)		40 [34]	33	-7	33	-7
(aminoguanidinium structure)		40 [34]	37	-3	36	-4
(triaminoguanidinium structure)		25 [34]	42	17	30	5
NH_4^+	(azido-triazolyl-tetrazolate anion structure)	20 [34]	7	-13	25	5
NH_4^+	(nitro-triazolyl-tetrazolate anion structure)	9 [34]	10	1	10	1
NH_3OH^+		2 [34]	4	2	4	2
(guanidinium structure)		20 [34]	16	-4	16	-4
(aminoguanidinium structure)		10 [34]	20	10	20	10
NH_4^+	(nitroimino-tetrazolate N-oxide anion structure)	10 [35]	14	4	15	5
$N_2H_5^+$		6 [35]	24	18	5	-1
NH_3OH^+		3 [35]	1	-2	2	-1

Cation	Anion	IS_{Exp} [J]	Eq. (1)	Dev	Eq. (2)	Dev
NH_3OH^+		8 [36]	12	4	12	4
NH_4^+		4 [36]	21	17	7	3
$N_2H_5^+$		9 [36]	16	7	17	8
		40 [36]	25	-15	34	-6
NH_4^+		40 [37]	42	2	40	0
NH_3OH^+		40 [37]	34	-6	33	-7
		40 [37]	42	2	41	1
		40 [37]	48	8	47	7
NH_3OH^+		10 [38]	3	-7	3	-7
$N_2H_5^+$		10 [38]	23	13	5	-5
NH_4^+		40 [38]	14	-26	33	-7
		40 [38]	23	-17	36	-4
		3 [38]	22	19	7	4
Root mean square (rms) deviation				11		6
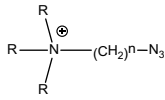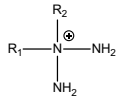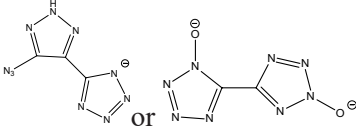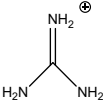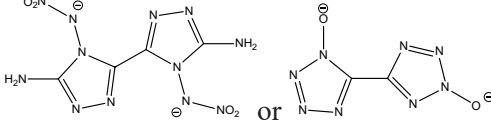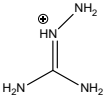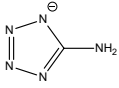
Beside the contribution of elemental compositions, the existence of some specific cations or anions may enhance or reduce the impact sensitivity in ionic molecular energetic materials. However, the effects of these specific anions or cations can be considered beside those variables given in Equation 1 through the following re-optimized correlation using the multiple linear regression method [23]:
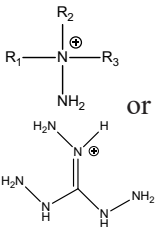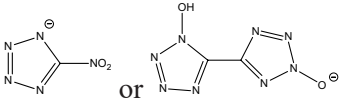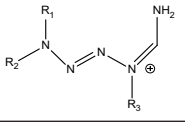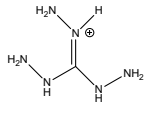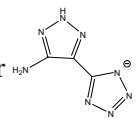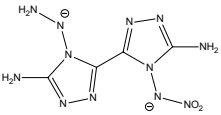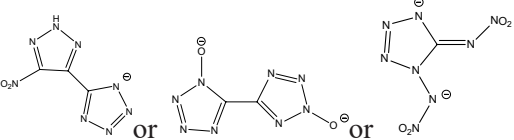
$$IS_{IL}^{corr}(J) = 35.04 + \frac{-1073(n_H)_{cat} + 728.9(n_H)_{cat} - 1761(n_O)_{cat} + 1032(n_C)_{ani} + 1061(n_H)_{ani} - 1261(n_N)_{ani} - 944.0(n_O)_{ani} + 3662 IS_{IL}^+ - 4291 IS_{IL}^-}{Mw} \quad (2)$$

where $IS_{IL}^{corr}(J)$ is the corrected impact sensitivity in J; IS_{IL}^+ and IS_{IL}^- are two correction functions that depend on stabilizing or destabilizing structural parameters in cations or anions. Indeed, the parameters IS_{IL}^+ and IS_{IL}^- show the

existence of specific cations or anions for correcting deviations of the number of atoms in Equation 1 from experimental data. The values of IS_{IL}^{+} and IS_{IL}^{-} are equal to 1.0 for the existence of specific cations or anions given in Table 2. The parameters IS_{IL}^{+} and IS_{IL}^{-} are equal to zero if the specified cations or anions in Table 2 are not satisfied. As indicated in Table 2, the kind of cations and anions is important for considering the contribution of IS_{IL}^{+} and IS_{IL}^{-}. For the same cation, the contribution of two different anions may give two different behaviors. For example, quaternary ammonium containing cations with the general formula $R_1R_2R_3N^{+}-NH_2$ gives IS_{IL}^{+} and IS_{IL}^{-} with two anions 5,5'-(hydrazine-1,2-diyl) bis(tetrazol-1-ide) and 5-nitrotetrazol-1-ide, respectively. The presence of two –NH– groups in 5,5'-(hydrazine-1,2-diyl)bis(tetrazol-1-ide) can provide $IS_{IL}^{corr}(J)$ because it was indicated that –NH$_2$ and >NH groups can decrease the sensitivity of an energetic compound with respect to impact stimuli [24]. Meanwhile, the attachment of a nitro group to the tetrazole ring in 5-nitrotetrazol-1-ide can increase its sensitivity.

Table 2.   The contribution of IS_{IL}^{+} and IS_{IL}^{-} in ionic liquids

IS_{IL}^{+}	
Cation	**Anion**
$R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N^{\oplus}}}-(CH_2)_n-N_3$	$N(NO_2)_2^{-}$
$R_1-\overset{\overset{R_2}{|}}{\underset{\underset{NH_2}{|}}{N^{\oplus}}}-NH_2$	$N(NO_2)(CN)^{-}$ or $C(NO_2)_2(CN)^{-}$ or NO_3^{-}
NH_4^{+}	or
$H_2N-\overset{\overset{NH_2}{|}}{C^{\oplus}}-NH_2$ (guanidinium)	or
$H_2N-\overset{\overset{NH_2}{|}}{\underset{\underset{NH_2}{|}}{C^{\oplus}}}$ (aminoguanidinium, HN)	

IS_{IL}^+	
Cation	**Anion**
	ClO_4^-
	$N(NO_2)_2^-$ or
NH_4^+	
$N_2H_5^+$	

Equations 1 and 2 may give large deviations for those ionic molecular energetic materials that have the following conditions:

(a) For the other classes of energetic ionic liquids, *e.g.* hydrazinium (picrylamino)-1,2,4-triazole [25] and hydroxylammonium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine [26].

(b) High oxygen content of cation, where a high value for the second term in Equation 1 can give a negative value of $IS_{IL}(J)$, *e.g.* (2,4,6-trinitrophenyl) guanidinium cation [27].

(c) Energetic metal salts such as silver salts with 5-aminotetrazole ligands [28].

2.2 Statistical evaluations of the new correlation

Tables 3 and 4 indicate the statistical parameters of Equations 1 and 2 corresponding to four and six variables in these equations, respectively. As can

be seen, these variables in both equations have a highly significant influence through their extremely small p-values and standard errors. The standard error of a coefficient is an important statistical parameter because it measures the precision of assessment of a coefficient where precision is measured by the standard deviation over repeated measurements. The p-value of a coefficient is the second important statistical parameter as it provides the probability threshold at which the null hypothesis would be rejected. Since all of the p-values are less than 0.05, the outcomes of the two new correlations are significant. Thus, the observed effect is not due to random variations. R-squared values or the coefficients of determination of Equations 1 and 2 are 0.685 and 0.908, respectively, which confirm the higher reliability of Equation 2. Equation 1 can be easily applied to the many energetic ionic liquids given in Table 1 because many of them do not have specific ionic liquids corresponding to IS_{IL}^+ and IS_{IL}^-. The existence of IS_{IL}^+ and IS_{IL}^- can decrease and increase IS_{IL}^{corr} (J) in Equation 2.

Table 3. Standardized coefficients and some statistical parameters of Eq. (1)

	Coefficients	Standard error	P-value	Lower bound (95%)	Upper bound (95%)
$(n_C)_{cat}/Mw$	30.50	8.10	3.65E-04	14.32	46.69
$(n_H)_{cat}/Mw$	-965.9	358.5	9.01E-03	-1682	-249.60
$(n_O)_{cat}/Mw$	756.2	155.2	7.55E-06	446.3	1066
$(n_C)_{ani}/Mw$	-1653	527	2.60E-03	-2706	-599.6
$(n_H)_{ani}/Mw$	1164	250	1.66E-05	664.6	1663
$(n_N)_{ani}/Mw$	1135	380	3.97E-03	376.4	1894
$(n_O)_{ani}/Mw$	-1233	181	4.03E-09	-1594	-870.9

Table 4. Standardized coefficients and some statistical parameters of Eq. (2)

	Coefficients	Standard error	P-value	Lower bound (95%)	Upper bound (95%)
$(n_C)_{cat}/Mw$	35.0	4.2	7.39E-12	26.73	43.36
$(n_H)_{cat}/Mw$	-1073	192	5.43E-07	-1456	-689.1
$(n_O)_{cat}/Mw$	728.9	82.0	1.14E-12	565.0	892.7
$(n_C)_{ani}/Mw$	-1761	287	6.59E-08	-2335	-1187
$(n_H)_{ani}/Mw$	1032	130	5.62E-11	771.0	1292
$(n_N)_{ani}/Mw$	1061	195	9.10E-07	672.1	1450
$(n_O)_{ani}/Mw$	-1261	94	4.73E-20	-1448	-1074
IS^+_{IL}/Mw	-944.0	115.7	2.12E-11	-1175	-712.6
IS^-_{IL}/Mw	3662	427	3.84E-12	2809	4514

Table 5.   Comparison of the predicted $IS_{IL}(J)$ and $IS_{IL}^{corr}(J)$ of several ionic liquids containing complex molecular structures by Eqs. (1) and (2) with the experimental data

Cation	Anion	IS_{Exp} [J]	Eq. (1)	Dev	Eq. (2)	Dev
(structure)	*(structure)*	25 [29]	32	7	33	8
(structure)	*(structure)*	8 [34]	26	18	12	4
(structure)	*(structure)*	40 [37]	44	4	43	3
Root mean square (rms) deviation				12		6

The differences in the predictions from the experiments for Equations 1 and 2 are also given in Table 1. As seen in Table 1, the root-mean-square (rms) deviations of Equations 1 and 2 are 11 J and 6 J, respectively, which also confirm the greater reliability of Equation 2. The estimated $IS_{IL}^{corr}(J)$ for Equation 2 are less than ±20 J for all 72 ionic liquids given in Table 1. Table 5 compares the predicted results of Equations 1 and 2 for a further three energetic ionic liquids containing complex structures. The rms deviations of Equations 1 and 2 are 12 J and 6 J, respectively. Thus, the new method can be used easily for any energetic ionic liquids containing complex structures. The values determined for the impact sensitivities of the ionic liquids depend on energetic cations or anions that might provide an active site for initiation of decomposition reactions. The new method can be useful for obtaining reliable impact sensitivities for energetic ionic liquids having a wide range of reported impact sensitivities.

3   Conclusions

It is an important problem for both chemists and the chemical industries to synthesize and develop safe energetic ionic liquids. An inability to predict the impact sensitivities of energetic ionic liquids can prevent the development of those compounds that have a high sensitivity with respect to external impact

stimuli. In contrast to the various approaches that are available for the prediction of the impact sensitivity of neutral energetic compounds, there is no method for the prediction of the impact sensitivity of energetic ionic liquids. The main intent of this work was to investigate the likelihood of a generalized method to correlate the impact sensitivities of energetic ionic liquids with their structures. It was shown that the impact sensitivity of an energetic ionic liquid depends on the elemental composition of both the cation and anion of a desired energetic ionic liquid divided by its molecular weight. The existence of some specific cations and anions is the other important factor that can be used to adjust the large deviations of impact sensitivities on the basis of elemental composition. As evident in Tables 1 and 5, the results predicted by Equation 2 show a higher reliability with respect to the experimental data as compared to Equation 1. Thus, the results of the current study indicate that the accuracy of the novel method is not necessarily enhanced by greater complexity.

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