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Research paper

Accurate Prediction of the Condensed Phase (Solid or Liquid) Heat of Formation of Triazolium-based Energetic Ionic Salts at 298.15 K

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Abstract: A novel method is introduced for the reliable prediction of the condensed phase (solid or liquid) heat of formation ($\Delta_f H^\theta$ (c)) of triazolium-based energetic ionic salts (EISs) at 298.15 K. It is based on the influence of some specific elemental compositions of cations and anions as additive parts. Two correcting functions, as non-additive quantities, are also used to adjust the first part. The coefficients of the specific elemental compositions of cations and anions in the new correlation, with a negative sign as well as a negative correcting function in the triazolium-based EISs, can decrease the value of $\Delta_f H^\theta$ (c) for the corresponding EISs. The reported $\Delta_f H^\theta$ (c) values of 57 different triazolium-based EISs were used to derive the new model. For 34 triazolium-based EISs, where the outputs of quantum mechanical methods were available, the Root Mean Squared Error (RMSE) of the new model was 156.0 kJ/mol. Meanwhile, the RMSE of complicated quantum mechanical methods is very large, *i.e.* 298.0 kJ/mol. The high reliability of the new model was also confirmed for a further 5 complex triazolium-based EISs as compared to the results of quantum mechanical calculations.

Keywords: heat of formation, condensed phase, triazolium-based, energetic ionic salt, safety

1 Introduction

Nitrogen-rich heterocycles, including imidazole, pyrazole, triazole, tetrazole, and 1,2,4,5-tetrazine, show a unique class of energetic molecular frameworks.

They have high heats of formation, density, and thermal stability. They also have high detonation and combustion performance as compared to the corresponding carbocyclic analogs [1-3]. Since energetic derivatives of nitrogen-rich heterocyclic materials have usually more than 50 wt.% nitrogen, they are called high nitrogen content (HNC) materials [4]. Different predictive methods can be used to design high-performance HNC explosives with desirable physicothermal, detonation and combustion properties as well as low sensitivities [3, 5-11]. Due to the importance of the condensed phase heats of formation of HNCs, several methods, including group additivities and quantitative structure-property relationships (QSPR), have been used in recent years [12-15]. For ionic salts (ISs), the presence of energetic anions or cations in some classes of ISs gives energetic ionic salts (EISs). EISs are most often composed of high nitrogen organic cations such as guanidinium, imidazolium, triazolium, and tetrazolium, as well as bulky anions with one or more energetic groups, *e.g.* $-NO_2$, $-N_3$, and $-CN$. Since EISs can have suitable thermally stability, they may be used as explosives, pyrotechnics or propellants [16-21]. In recent years, considerable effort has been devoted to the introduction of reliable models for the prediction of the physical and thermodynamic properties of some kinds of EISs, *e.g.* density [22-25], decomposition temperature [26] and melting point [27, 28].

It is important to design new EISs with desirable properties, and a unique architectural platform for developing new predictive methods is required. Since there are different interionic interactions in the condensed phase of EISs as compared to their gaseous state, predicting the condensed phase (solid or liquid) heat of formation ($\Delta_f H^\theta$ (c)) of different classes of EISs at room temperature, *i.e.* 298.15 K, may be difficult. The purpose of the present work was to introduce a novel approach for the prediction of $\Delta_f H^\theta$ (c) values of triazolium-based EISs. For some triazolium-based EISs, where the outputs from complex quantum mechanical methods were also available, the accuracy of the novel proposed model was tested and compared.

2 Deriving the New Model

For neutral organic compounds containing energetic groups, it was found that elemental composition makes an important contribution to the estimation of their $\Delta_f H^\theta$ (c) values [12-18]. Moreover, particular molecular fragments and functional groups, besides elemental composition, have an important role in the prediction of $\Delta_f H^\theta$ (c) values [13-17]. The study of $\Delta_f H^\theta$ (c) values of triazolium-based EISs has shown that the elemental composition of the cations and anions, as well

as the contributions of some specific cations and anions, can be used to derive a suitable correlation. Among the different elements in cations and anions, only some of the atoms have effective contributions, which can increase the coefficient of determination (R^2).

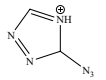
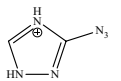
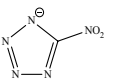
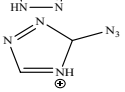
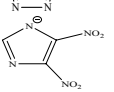
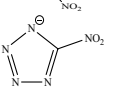
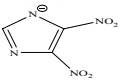
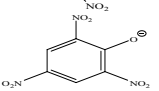
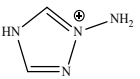
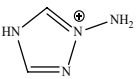
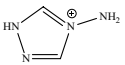
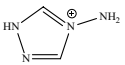
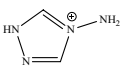
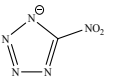
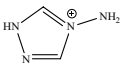
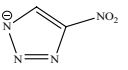
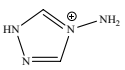
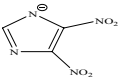
Experimentally determined $\Delta_f H^\theta$ (c) values of triazolium-based EISs were collected from various sources. They included 57 triazolium-based EISs. Due to the existence of reported values from complex quantum mechanical approaches for 34 triazolium-based EISs, the predicted results were also compared with the outputs from these quantum mechanical methods. The experimental values of 5 molecules containing complex triazolium-based EISs were also chosen for external validation of the new model. The reported values of $\Delta_f H^\theta$ (c) for 57 different triazolium-based EISs are listed in Table 1. They contain different types of energetic anions, which were used to derive the new model. The multiple linear regression method [29] was used to find the optimized model as:

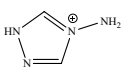
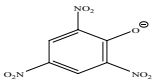
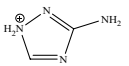
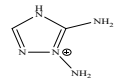
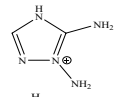
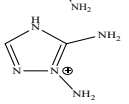
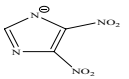
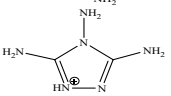
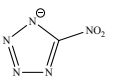
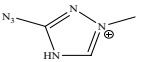
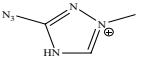
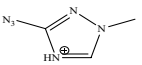
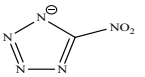
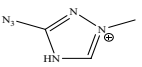
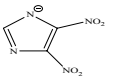
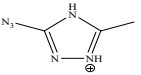
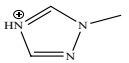
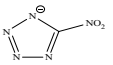
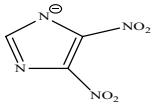
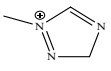
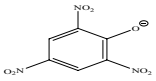
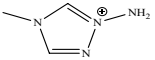
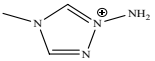
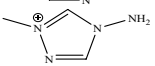
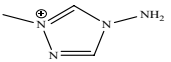
$$\Delta_f H^\theta \text{ (c)} = -27.31H_{cat} + 102.7N_{cat} + 259.8C_{ani} - 319.2H_{ani} + 45.32N_{ani} - 125.9O_{ani} + 632.6Cl_{ani} + 79.78\,\Delta_f H^\theta_{Inc} - 74.50\,\Delta_f H^\theta_{Dec} \quad (1)$$

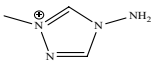
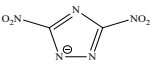
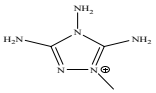
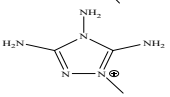
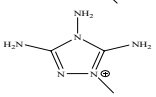
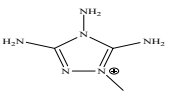
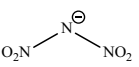
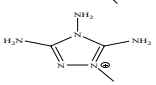
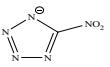
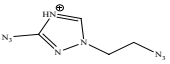
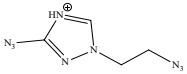
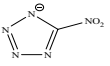
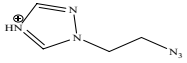
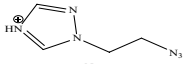
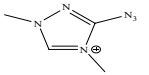
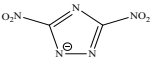
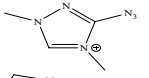
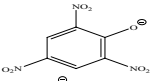
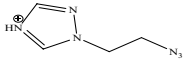
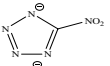
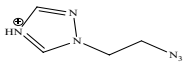
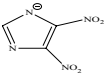
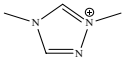
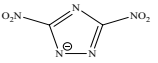
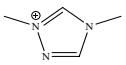
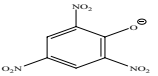
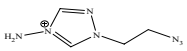
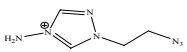
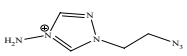
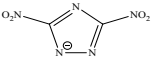
where H_{cat} and N_{cat} represent the number of hydrogen and nitrogen atoms in the cation, respectively; C_{ani}, H_{ani}, N_{ani}, O_{ani} and Cl_{ani} the number of carbon, hydrogen, nitrogen, oxygen and chlorine atoms in the anion, respectively; whilst $\Delta_f H^\theta_{Inc}$ and $\Delta_f H^\theta_{Dec}$ give increasing and decreasing functions in the triazolium-based EISs, respectively. For the design of high detonation or combustion performance compounds, it is desirable to choose those materials with high positive heats of formation [3, 5-10, 30]. Coefficients in Equation 1 show the contributions of the different variables for obtaining a high heat content in triazolium-based EISs. Thus, variables with high positive and low negative coefficients can give large positive values of $\Delta_f H^\theta$ (c). Different available methods have confirmed that elemental composition has an important contribution for the prediction of the heats of formation of different classes of compounds [31-37]. As seen in Equation 1, there is no contribution for the presence of some atoms in the cations or anions, such as the number of carbon and oxygen atoms in the cation, because their presence cannot improve R^2. Two parameters, $\Delta_f H^\theta_{Inc}$ and $\Delta_f H^\theta_{Dec}$, can adjust large deviations of the measured $\Delta_f H^\theta$ (c) values from those predicted by the elemental composition. Thus, these two parameters, $\Delta_f H^\theta_{Inc}$ and $\Delta_f H^\theta_{Dec}$, can improve the predicted heat content based on the contributions of H_{cat}, N_{cat}, C_{ani}, H_{ani}, N_{ani}, O_{ani} and Cl_{ani} in Equation 1 for the existence of some specific cations and anions, which are listed in Table 2. The heat content of a desired triazolium-based EIS can be increased and decreased by the inclusion

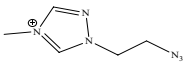
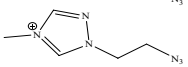
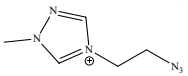
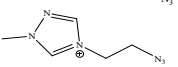
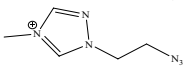
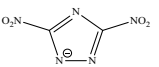
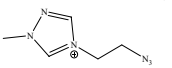
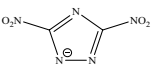
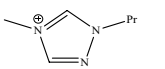
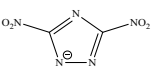
of $\Delta_f H^{\theta}_{Inc}$ and $\Delta_f H^{\theta}_{Dec}$, respectively. For a specific anion listed Table 2, the kind and number of substituents attached to a triazole ring can decrease and increase interionic attractions, which are specified by considering $\Delta_f H^{\theta}_{Inc}$ and $\Delta_f H^{\theta}_{Dec}$, respectively. Figure 1 shows the correlation of predicted $\Delta_f H^{\theta}$ (c) values versus experimental data.

Table 1. Predictions of $\Delta_f H^{\theta}$ (c) [kJ/mol] by Equation 1 and quantum mechanical methods for EISs based on triazolium cations as compared to experimental data

Cation	Anion	Exp.[a]	New model	Dev.[c]	Q.M. methods	Dev.[c]
	NO_3^-	218.8 [42]	201.9	–16.9	252.3[42][b]	33.5
		979.9 [42]	968.3	–11.6	734.3 [42][b]	–245.6
		401.7 [42]	411.5	9.8	525.1 [42][b]	123.4
		409.6 [42]	433.5	23.9	366.1 [42][b]	–43.5
		503.3 [42]	456.5	–46.8	162.8 [42][b]	–340.6
		497.9 [42]	493.8	–4.1	–84.9 [42][b]	–582.8
	NO_3^-	34.7 [42]	–58.1	–92.8	–25.1 [42][b]	–59.8
	ClO_4^-	356.9 [42]	403.3	46.4	17.2 [42][b]	–339.7
	NO_3^-	–109.6 [42]	–58.1	51.5	–4.2 [42][b]	105.4
	ClO_4^-	298.3 [42]	291.5	–6.8	38.1 [42][b]	–260.2
		702.1 [42]	708.3	6.2	466.9 [42][b]	–235.1
		141.4 [42]	143.4	1.9	368.2 [42][b]	226.8
		466.5 [42]	412.2	–54.3	274.5 [42][b]	–192.0

		469.0 [42]	449.5	–19.5	24.3 [42][b]	–444.8
	NO_3^-	–171.1 [43]	–169.9	1.2	-	-
	NO_3^-	–89.5 [42]	–94.5	–5.0	–56.1 [42][b]	33.5
	ClO_4^-	484.5 [42]	478.7	–5.8	–15.5 [42][b]	–500.0
		405.8 [42]	487.6	81.7	217.6 [42][b]	–188.3
		528.0 [44]	510.6	–17.4	-	-
	NO_3^-	93.3 [42]	147.3	54.0	224.7 [42][b]	131.4
	ClO_4^-	574.9 [42]	608.7	33.8	263.2 [42][b]	–311.7
		1085.3 [42]	1113.1	27.8	702.9 [42][b]	–382.4
		700.8 [42]	617.6	–83.2	492.0 [42][b]	–208.8
	NO_3^-	156.5 [42]	147.3	–9.2	194.6 [42][b]	38.1
		808.3 [42]	777.7	–30.6	325.1 [42][b]	–483.3
		80.3 [42]	95.9	15.6	132.2 [42][b]	51.9
		409.6 [42]	439.2	29.6	–118.8 [42][b]	–528.4
	NO_3^-	–160.2 [42]	–112.8	47.5	–22.6 [42][b]	137.7
	ClO_4^-	544.8 [42]	548.1	3.3	2.5 [42][b]	–542.2
	NO_3^-	–172.8 [42]	–112.8	60.0	–13.0 [42][b]	159.8
	ClO_4^-	215.1 [42]	236.9	21.8	11.7 [42][b]	–203.3

		378.2 [42]	350.5	–27.7	303.3 [42][b]	–74.9
		530.6 [45]	506.3	–24.3	-	-
	NO_3^-	64.2 [45]	38.0	–26.2	-	-
	ClO_4^-	498.4 [45]	499.4	1.0	-	-
		276.3 [45]	242.1	–34.2	-	-
		519.0 [45]	605.0	86.0	-	-
	NO_3^-	437.2 [46]	428.0	–9.2	-	-
		1138.7 [46]	1194.4	55.7	-	-
	NO_3^-	27.2 [46]	92.6	65.4	-	-
	ClO_4^-	426.2 [46]	442.3	16.1	-	-
		792.9 [42]	787.3	–5.5	544.8 [42][b]	–248.1
		611.3 [42]	600.3	–11.0	213.8 [42][b]	–397.5
		676.0 [46]	659.6	–16.4	-	-
		380.2 [46]	376.7	–3.5	-	-
		118.0 [42]	108.8	–9.2	173.6 [42][b]	55.6
		340.2 [42]	384.6	44.4	–139.3 [42][b]	–479.5
	NO_3^-	321.1 [46]	327.6	6.5	-	-
	ClO_4^-	828.4 [46]	828.9	0.5	-	-
		331.7 [47]	333.3	1.6	-	-

	NO_3^-	66.3 [46]	38.0	–28.3	-	-
	ClO_4^-	568.0 [46]	499.4	–68.6	-	-
	NO_3^-	77.7 [46]	38.0	–39.7	-	-
	ClO_4^-	541.1 [46]	499.4	–41.7	-	-
		395.2 [47]	389.5	–5.7	-	-
		771.3 [47]	732.7	–38.6	-	-
		198.7 [47]	223.0	24.3	-	-

[a] The experimental condensed phase standard enthalpy of formation; [b] Calculated by the MP2/aug-cc-pV*n*Z//B3LYP/TZVP method; [c] Deviation from experimental value.

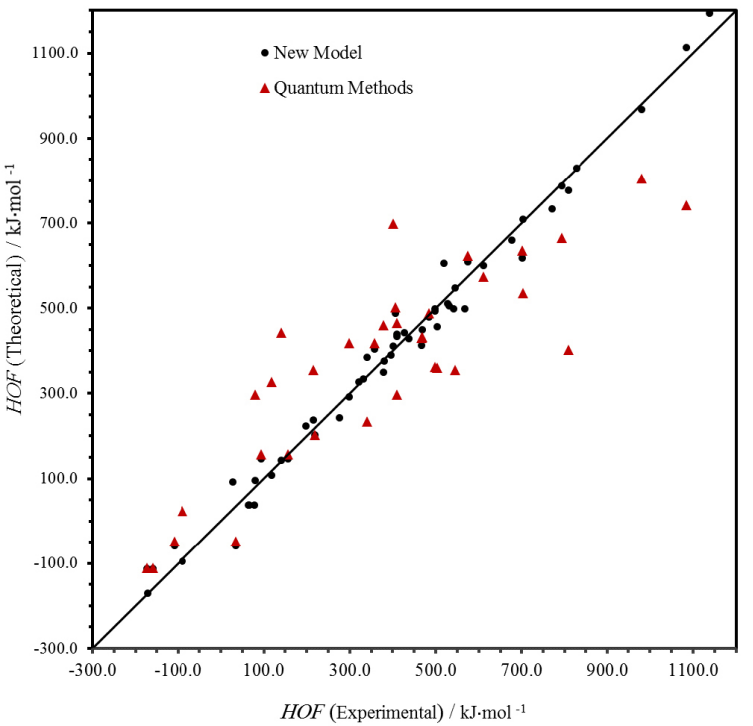
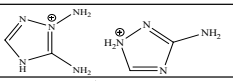
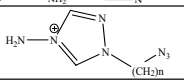
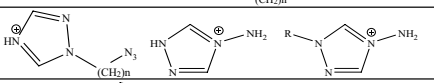
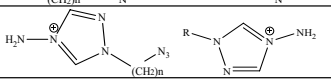
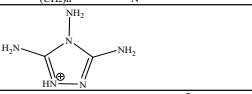
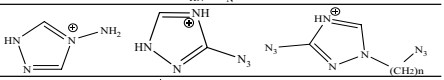
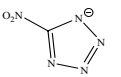
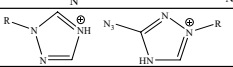
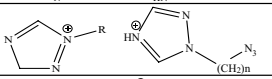
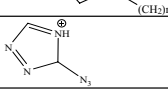
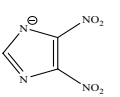
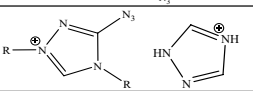
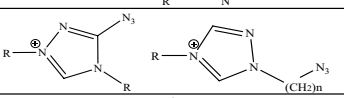
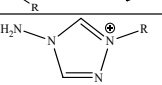
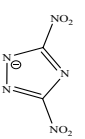
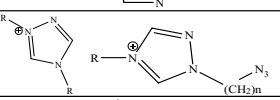
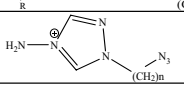
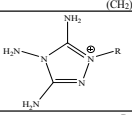
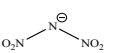
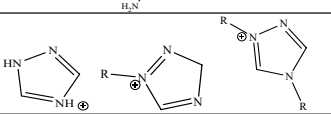
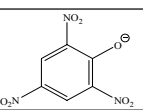
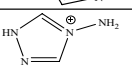
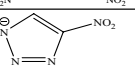


Figure 1. Correlation of predicted $\Delta_f H^\theta$ (c) values of EISs versus experimental data

Table 2. Contribution of structural parameters in predicting $\Delta_f H^\theta$ (c)

Cation	Anion	$\Delta_f H^\theta_{Inc}$	$\Delta_f H^\theta_{Dec}$
	NO_3^-	0	1.5
		2.0	0
	ClO_4^-	0	1.5
		2.5	0
		0	2.0
		2.5	0
		5.0	0
		0	2.5
		0	3.5
		1.5	0
		1.5	0
		0	1.5
		0	3.0
		0	5.5
		3.0	0
		1.5	0
		0	3.5

3 Results and Discussion

3.1 Statistical parameters of the novel model

Table 3 lists the statistical evaluations of Equation 1 corresponding to the elemental composition of the cations and anions, as well as the correcting functions for triazolium-based EISs. These data allow a comparison of the relative contributions of the variables in Equation 1. It also provides regression coefficients of the variables, standard errors (sd), *P*-value (significance), and confidence intervals of Equation 1. The standard error shows a measure of the precision of the evaluation of a coefficient in which precision is measured by the standard deviation over the repeated quantities. The *P*-value gives the probability that a parameter estimated from the measured values should have the value which was determined. If the *P*-value of a coefficient is less than 0.05, the effect is significant and the observed effect is not due to random variations. As seen in Table 3, each of the variable in Equation 1 has a highly significant impact, as evidenced by their extremely small *P*-values and standard errors. Since the *P*-values for the coefficients of some elements in cations and anions are greater than 0.05, their presence cannot change the value of R^2 of Equation 1. Equation 1 has a simple form and can be easily used for different triazolium-based EISs. As may be seen in Equation 1 and Table 3, the coefficients of N_{cat}, C_{ani}, N_{ani} and Cl_{ani} have positive signs, which confirms an increasing effect on the $\Delta_f H^\theta$ (c) value. The effect of changing C_{ani} and Cl_{ani} on $\Delta_f H^\theta$ (c) is greater than N_{cat} and N_{ani}, because the contribution of their coefficients is more than doubled. By contrast, the coefficients of H_{cat}, H_{ani} and O_{ani} have negative values, which confirms that low values of these coefficients can increase the value of $\Delta_f H^\theta$ (c). Thus, increasing and decreasing values of $N_{cat} + C_{ani} + N_{ani} + Cl_{ani}$ and $H_{cat} + H_{ani} + O_{ani}$, respectively, offers an important outcome for gaining high positive values of $\Delta_f H^\theta$ (c).

The existence of some specific cations and anions for increasing and reducing the energy content is also important in Equation 1 by considering the contributions of both $\Delta_f H^\theta_{Inc}$ and $\Delta_f H^\theta_{Dec}$. The presence of $–NH_2$ or >NH groups in the cations is especially important because they cannot only increase the thermodynamic stability but also decrease the sensitivities to different stimuli such as impact, electric spark and shock [3, 38, 39]. As indicated in Tables 1 and 2, selection of some specific cations and anions can improve the values of $\Delta_f H^\theta_{Inc}$ and $\Delta_f H^\theta_{Dec}$. Thus, the existence of $\Delta_f H^\theta_{Dec}$ in triazolium-based EISs can enhance their thermodynamic instability.

Table 3. Regression coefficients of Equation 1, as well as their standard deviations (sd), P-values, and confidence intervals

Descriptor	Coefficient	sd	P-value	Lower bound (95%)	Upper bound (95%)
H_{cat}	–27.31	3.15	2.17×10^{-11}	–36.65	–20.98
N_{cat}	102.7	3.8	1.27×10^{-30}	95.02	110.4
C_{ani}	259.8	16.5	1.50×10^{-20}	226.6	293.1
H_{ani}	–319.2	34.6	3.27×10^{-12}	–388.8	–249.7
N_{ani}	45.32	6.36	4.82×10^{-9}	32.52	58.11
O_{ani}	–125.9	7.7	2.57×10^{-21}	–141.3	–110.4
Cl_{ani}	632.6	19.6	3.70×10^{-34}	593.1	672.1
$\Delta_f H^{\theta}_{Inc}$	79.78	5.20	3.88×10^{-20}	69.32	90.23
$\Delta_f H^{\theta}_{Dec}$	–74.50	5.17	4.74×10^{-19}	–84.90	–64.10

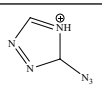
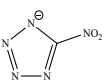
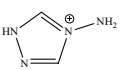
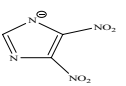
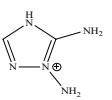
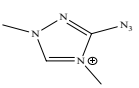
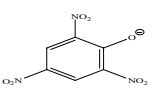
3.2 Assessment of Equation 1 compared to quantum mechanical approaches

Table 1 shows a comparison between the statistical parameters of Equation 1 and quantum mechanical methods. R^2 mainly reflects the goodness of fitting and is equal to 0.9942 for all of the 57 data points listed in Table 1. That the value of R^2 is close to 1.0 indicates that we have accounted for almost all of the variability with the variables specified in the model. R^2 is a very useful statistical parameter of the model, but attending to it alone may be misleading [40]. Moreover, the standard deviation of the model provides the model error, equal to 40.63, where $F = 919.1$ and significance $F = 1.08\times10^{-49}$. Since the calculated data by complex quantum mechanical methods were available for only 34 of the data given in Table 1, comparison of the statistical parameters for these data were also reported in Table 4. The Root Mean Squared Error (RMSE) is independent of the distribution of the data points and provides a reliable indication of the fitness of the model. For good models, RMSE values should be low and as similar as possible to ensure both predictive ability (low values) and generalizability (similar values) [41]. Mean Absolute Error (MAE) measures the deviations and indicates the average size of the errors when negative signs are ignored. Maximum of Errors (Max Error) determines the worst error that occurred in the estimations, which can be regarded as a measure of precision. As indicated in Table 4, the calculated RMSE, MAE and Max Error of the new model are surprisingly much less than those of the quantum mechanical approaches. As seen in Table 5, the reliability of the new model was also tested for a further 5 complex triazolium-based EISs with different highly energetic anions, where the outputs of quantum mechanical methods were also available.

Table 4. Performance statistics of Equation 1 as compared to quantum mechanical predictions

Method	Data-points	RMSE	MAE	Max Error	R^2	sd	F statistic	Signifi-cance F
Eq. (1)	57	37.28	28.27	92.85	0.9942	40.63	919.1	1.08×10^{-49}
	34	156.0	122.4	406.4	--	--	--	--
Q.M. methods	34	298.0	246.8	582.8	--	--	--	--

Table 5. Predictions of $\Delta_f H^\theta$ (c) (in kJ/mol) Equation 1 and quantum mechanical methods for 5 complex EISs based on triazolium cations as compared to experimental data

Cation	Anion	Exp.[a]	New model	Dev.[c]	Q.M. methods	Dev.[c]
	NO_3^-	218.8 [42]	201.9	–16.9	252.3 [42][b]	33.5
		409.6 [42]	433.5	23.9	366.1 [42][b]	–43.5
		466.5 [42]	412.2	–54.3	274.5 [42][b]	–192.0
	ClO_4^-	484.5 [42]	478.7	–5.8	–15.5 [42][b]	–500.0
		611.3 [42]	600.3	–11.0	213.8 [42][b]	–397.5

[a] The experimental condensed phase standard enthalpy of formation; [b] Calculated by the MP2/aug-cc-pV*n*Z//B3LYP/TZVP method; [c] Deviation from experimental value.

4 Conclusions

A novel approach has been introduced to forecast $\Delta_f H^\theta$ (c) values of triazolium-based EISs on the basis of elemental composition and two correcting functions. Equation 1 has been derived on the basis of some specific elemental compositions of cations and anions as well as $\Delta_f H^\theta_{Inc}$ and $\Delta_f H^\theta_{Dec}$. The high reliability of Equation 1 has been confirmed by various statistical parameters. Equation 1 also gives a new route for designing triazolium-based EISs with desirable

$\Delta_f H^\theta$ (c) values. The current work provides surprisingly more reliable results than those obtained by complex quantum mechanical methods. Due to the large experimental errors in the determination of $\Delta_f H^\theta$ (c) values for various EISs, the predicted results from the present method are satisfactory.

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