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Imidazolium based energetic ionic liquids for monopropellant applications: A theoretical study

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A large variety of 1-ethyl-3-methylimidazolium ([EMIm]⁺) based energetic ionic liquids (ILs) have been studied by their ion pair ([EMIm]⁺[X]⁻) formation using high accuracy G3MP2 method and density functional theory (DFT) methods M06L, M05-2X, M06-2X and B3LYP. The selected X⁻ includes nitrogen rich derivatives of tetrazolate and triazolate, dinitramine, dicyanamide as well as conventional anions BF₄⁻ and PF₆⁻. The nitrogen enrichment in the system produces energetic ionic liquids (EILs) which showed comparable and in some cases superior thermochemical, fluid and specific impulse (Isp) properties than conventional ionic liquids. The binding energy values for [EMIm]⁺[X]⁻ are in the range 336 – 400 kJ/mol at DFT while the atomization procedure used to compute their heat of formation ($\Delta_f H^0$) at G3MP2 level produced results very close in agreement with available experimental data (maximum deviation < 5 %). The $\Delta_f H^0$ of conventional ILs is negative whereas that of EILs (167 - 559 kJ/mol) confirmed their high energy state. The predicted Isp of all EILs are slightly lower compared to hydrazine in monopropellant systems whereas a significant increase in Isp is observed with the addition of hydroxyl ammonium nitrate (HAN). A good linear correlation between Isp and the weight % of (N + O) content of the EIL is also observed. Our results suggest that imidazolium based energetic ionic liquids have attractive thermochemical properties to be used as green substitute to hazardous hydrazine for monopropellant application in spacecraft technology.

1. Introduction

Hydrazine is one of the most widely used monopropellants for spacecraft application due to its good combustion, decomposition and storage properties.¹ However, owing to high toxic and carcinogenic character of this compound, development of new energetic and green compounds which show higher propellant performance than hydrazine is necessary. Ionic salts are attractive for this purpose as they are essentially non-volatile and thermally stable under normal conditions.²⁻⁴ The energetic salts such as, hydroxyl ammonium nitrate (HAN), ammonium dinitramide (ADN) and hydrazinium nitroformate^{1,5} were proposed as a substitute for hydrazine. However they have melting points above room temperature, and can be used only in an aqueous solution to produce a storable liquid propellant. Recently Ionic Liquids (ILs) have been anticipated, as the new generation green propellant fuels.⁶⁻¹⁰ ILs are more attractive than ionic salts as they show low melting points, thus potentially combining the useful characteristics of salt systems with the advantage of handling liquid systems. Their low sensitivity to external stimuli such as impact, friction, shock, and electrostatic discharge further add to the credit.¹¹

Among various ILs in use, imidazolium based ILs are known for their chemical stability and fluid properties. The unique properties of these cations stem from the electronic structure of the aromatic

cations. The electronic structure of imidazolium cations is characterized by 3-center-4-electron configuration across the N1-C2-N3 bonds, and a double bond between C4 and C5. The C2 is positively charged owing to the electron scarcity in the C=N bond, imparting slight acidity to the C2-H hydrogen atom (Fig. 1). Hence the C2-H⁺ anion interactions play an important role in the overall chemical and physical properties of the compound. The liquescency features of imidazolium based ILs is also well explained with these C2-H⁺ anion interactions¹² and are relevant to storability of these compounds as propellants. Apart from fluidity parameters, heat of formation ($\Delta_f H^0$) turns out to be a decisive factor for propellant properties. The energy release during combustion of a high energy material is given by the difference between the heat of formation of the compound and that of the combustion products which increases with increasing positive heat of formation of the compound. In spite of the innumerable reports on structure-physical property correlation of ILs,¹³⁻¹⁵ studies on the thermo chemical properties are very limited. Recently, ab initio methods have been employed for accurate calculation of heat of formation parameters of energetic salts.^{16,17} Heintz et al.¹⁸ studied heat of formation of the ionic liquid 1-butyl-3-methylimidazolium dicyanamide (BMImdc) using atomization reaction and isodesmic reactions and observed a concurrence between theoretical and experimental results. In the present study, the formation and stabilities of several 1,3 dialkyl substituted imidazolium based ILs are predicted using DFT and ab initio calculations. The ILs and a binary mixture of ionic liquid with an oxidizer are explored and the performance is compared with that of hydrazine.

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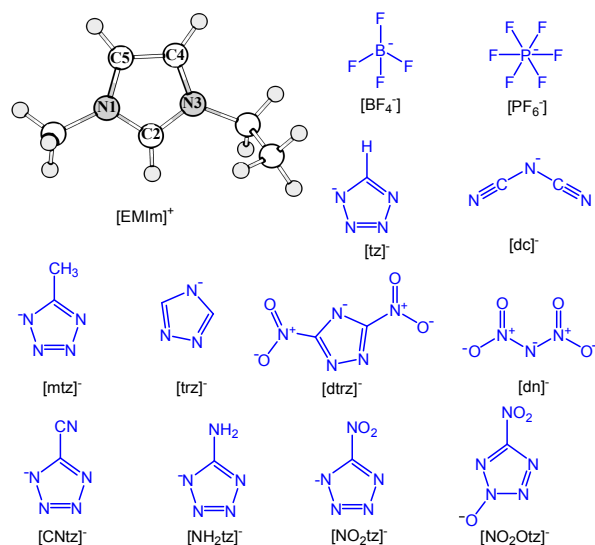
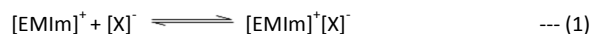


Fig. 1 Chemical structures of imidazolium cation and the selected counter anions. The abbreviations used to name these systems are also given.

2. Methodology

The most widely used 1-ethyl-3-methylimidazolium cation ([EMIm]⁺) is selected as the cationic portion of the IL while twelve different anions are selected to form ion-pair complexes with the cation (Fig. 1). Among the anions, tetrafluoroborate (BF₄⁻) and hexafluorophosphate (PF₆⁻) are conventionally used anions while the rest of them are classified as nitrogen rich energetic anions. Among the nitrogen rich anions, the tetrazolate anions [tz] and its derivatives are given prime importance as they possess high heats of formation resulting from the nitrogen-nitrogen bonds, ring strain, and high energy density.¹⁹⁻²¹ In addition, the aromatic ring of [tz] provides the required thermal stability for its ion pairs. To improve the oxygen balance in [tz], the NO₂ substitution is useful. The study also includes the anion 5-nitrotetrazolate-2N-oxide ([NO₂Otz]) synthesized by Klapötke et al. as a superior energetic anion than nitrotetrazole.²²

The dispersion included Minnesota DFT method M06L²³ as implemented in *Gaussian09*²⁴ is used in conjunction with 6-311+G(d,p) basis set for optimizing all the molecular geometries in their gas phase. Since the focus of this study is on the propellant applications of energetic ionic liquids (EILs) and considering that the process of ignition and combustion of EILs takes place in the gas phase, the gas phase results are expected to be reliable. Very recently, a benchmark study by Remya and Suresh showed that this method is the most effective to reproduce CCSD(T) level geometry and binding energy (*E_b*) of noncovalently bonded molecular dimers of organic molecules.²⁵ Several orientations of the anion-cation pairs were considered to locate the most stable IL structure (ESI). Normal modes of vibrations were analyzed for all the optimized geometries to ensure that every structure is a minimum on the potential energy surface. Basis set superposition error corrected *E_b* of the ion pair [EMIm]⁺[X]⁻ formation in the gas phase (eqn. 1) was calculated at M06L/6-311+G(d,p) level.



In the present study, atomization data obtained from the literature along with the G3MP2 level thermodynamic data is used to calculate the heat of formation for all IL systems. The G3MP2 is one of the popular high accuracy methods for calculating enthalpy quantities which is based on complex energy computations involving several pre-defined calculations on the specified molecular system.²⁶

Calculating enthalpies of formation of the molecule at 298K, $\Delta_f H^\circ(M, 298\text{K})$ can be split into a couple of steps which is given below.²⁷

(a) Atomization energy of the molecule, $\sum D_o(M)$

$$\sum D_o(M) = \sum n_i X(\epsilon_o) - M(\epsilon_o + \text{ZPE}) \quad \text{--- (2)}$$

M stands for the molecule and X to represent each element which makes up M, n is the number of atoms of X in M. ϵ_o is the electronic energy and ZPE is the zero-point energy.

(b) Heat of formation of the molecule at 0K, $\Delta_f H^\circ(M, 0\text{K})$

$$\Delta_f H^\circ(M, 0\text{K}) = \sum n_i \Delta_f H^\circ(X, 0\text{K}) - \sum D_o(M) \quad \text{--- (3)}$$

The experimental values of $\Delta_f H^\circ(X, 0\text{K})$ of the first and second row atomic elements at 0K are tabulated in Table 1.

(c) Enthalpy correction for the molecule, $H_M^\circ(298\text{K}) - H_M^\circ(0\text{K})$

$$H_M^\circ(298\text{K}) - H_M^\circ(0\text{K}) = H_{\text{corr}} - M(\epsilon_{\text{ZPE}}) \quad \text{--- (4)}$$

The enthalpy corrections, $H^\circ(298\text{K}) - H^\circ(0\text{K})$ is used to convert the atomic heats of formation at 0 K to those at 298.15 K, which is obtained from Gaussian output as "thermal correction to enthalpy".

(d) Heat of formation of the molecule at 298K, $\Delta_f H^\circ(M, 298\text{K})$.

$$\Delta_f H^\circ(M, 298\text{K}) = \Delta_f H^\circ(M, 0\text{K}) + [H_M^\circ(298\text{K}) - H_M^\circ(0\text{K})] - [\sum n_i (H^\circ(298\text{K}) - H^\circ(0\text{K}))] \quad \text{--- (5)}$$

Table 1: Experimental enthalpies of formation of elements (kcal/mol) and enthalpy correction taken for elements in their standard states.

Element	$\Delta_f H^\circ(X, 0\text{K})^{28}$	$H^\circ(298\text{K}) - H^\circ(0\text{K})^{28}$
H	51.63	1.01
Li	37.69	1.10
Be	76.48	0.46
B	136.20	0.29
C	169.98	0.25
N	112.53	1.04
O	58.99	1.04
F	18.47	1.05
Na	25.69	1.54
Mg	34.87	1.19
Al	78.23	1.08
Si	106.6	0.76
P	75.42	1.28
S	65.66	1.05
Cl	28.59	1.10

To estimate the accuracy of the proposed methods, an error function based on the normalized standard deviation is calculated as follows (eqn.6),

$$\Delta q(\%) = \sqrt{\frac{\sum[(\Delta_f H^o(\text{exp}) - \Delta_f H^o(\text{cal})) / \Delta_f H^o(\text{exp})]^2}{(N-1)}} \quad \text{---(6)}$$

where $\Delta q(\%)$ is the normalized standard deviation. The $\Delta_f H^o(\text{exp})$ and $\Delta_f H^o(\text{cal})$ are the experimental and calculated heat of formation. N is the number of data points available. The gaseous heat of formation, $\Delta_f H^o$ is also calculated using B3LYP/6-311+G(d,p), M06L/6-311+G(d,p), M05-2X/6-311+G(d,p) and M06-2X/6-311+G(d,p) levels of DFT.

The term 'specific impulse' (Isp) is used in rocket propulsion to define the impulse created per unit weight of propellant. It is equal to the number of pounds of thrust produced per pound of propellant burned per second. Isp is usually expressed in "seconds". Using the G3MP2 level heat of formation of the molecule, rocket performance analysis is done to determine the capability of the selected ILs (combination of $[\text{EMIm}]^+$ and any of the selected anions) to function as chemical monopropellants. Equilibrium combustion analysis is done by using the NASA Chemical Equilibrium with Applications (CEA) computer code.²⁹ Isp is calculated by assuming equilibrium composition during expansion from infinite area combustor. CEA is employed for 100 % fuel and then with a shifting equilibrium assumption for binary mixture, fuel and oxidiser. In the binary mixture of IL with HAN, Isp is calculated as a function of percent oxidiser by weight.

3. Results and Discussion

3.1 Electronic structure and properties

To locate various conformers of the imidazolium cation-heterocyclic anion complex, the anion is initially placed above the π -region of the cation so that the distance between the center of the heterocycles is ~ 3.5 Å, a typical value for π - π aromatic interactions. Further, in various starting point geometries, each of the ring atoms of the anion is allowed to interact closely with the C2-H hydrogen of the imidazolium ring at distances around 3.0 - 3.5 Å. For open chain anions, viz. [dc] and [dn], the central atom (N) of the anion is placed over the center of the imidazolium cation approximately ~ 3.5 Å while keeping the orientation of the end positions near to the ethyl or methyl substituents of the cation. Apart from the π - π stacking type initial structures for geometry optimization, the in-plane orientation of the ion-pair complexes is also considered wherein the anion is placed close to the C2-H region of the imidazolium cation. The $[\text{EMIm}]^+$ showed two distinct nearly isoenergetic conformations with energy difference 0.30 kJ/mol (ESI). Hence, both the conformers are used for generating initial structures of ion-pair complexes. The conformational space scanned for all the ion-pair geometries are presented in the ESI. The most stable structures of the representative energetic ion pairs $[\text{EMIm}]^+[\text{X}]^-$ are reported in Fig. 2. All of them exhibit non-covalent C-H...C/C-H...N/C-H...O interactions in the range 2.17 Å - 2.64 Å. Normally, if uncharged systems are involved, such noncovalent distances would suggest very weak E_b in the range 10 - 20 kJ/mol. In sharp contrast to this, the non-covalent E_b computed for IL systems are very high, in the range 336 - 400 kJ/mol (Table 2) indicating that strong electrostatic interactions prevail in all the charge separated ion pairs.

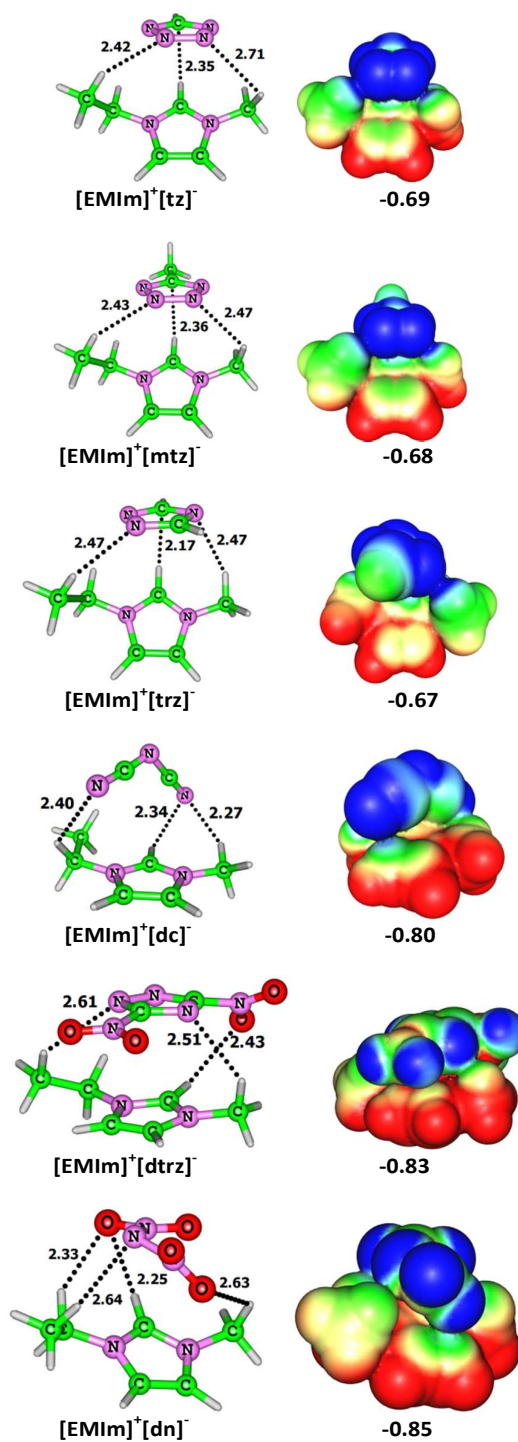


Fig. 2 The optimized structures (left) of the representative set of EILs predicted for propellant applications and MESP plots (right). MESP-derived charge on anion is also depicted. Distances in Å.

The cation-anion charge separation is significant in all the cases which is well evident in the molecular electrostatic potential (MESP) plots given in Fig. 2, where the anion has the MESP-derived Merz-Singh-Kollman (MK) charge in the range of -0.68 to -0.86 (Table 2) and cation has the counter positive values. The MK charge can be considered as a measure of the amount of charge transfer from the

anion to the cation. The charge transfer (29 – 34 %) is clearly more dominant in four energetic anions, viz. [trz]⁻, [tz]⁻, [mtz]⁻ and [NH₂tz]⁻ which show E_b in the range 388 – 400 kJ/mol while the rest of the energetic anion show E_b in the range 336 – 370 kJ/mol with charge transfer 20 ± 5 %

Table 2. Binding energy E_b , ΔE^* and MK charge of ion pairs computed at M06L/6-311+G level of DFT.

IL	E_b (kJ/mol)	ΔE^* (eV)	MK charge
[EMIm] ⁺ [BF ₄] ⁻	370.0	5.38	-0.86
[EMIm] ⁺ [PF ₆] ⁻	351.2	5.54	-0.85
[EMIm] ⁺ [dc] ⁻	361.9	2.83	-0.80
[EMIm] ⁺ [trz] ⁻	398.7	3.31	-0.67
[EMIm] ⁺ [dtrz] ⁻	335.5	3.14	-0.83
[EMIm] ⁺ [dn] ⁻	355.9	3.30	-0.85
[EMIm] ⁺ [tz] ⁻	388.0	3.68	-0.69
[EMIm] ⁺ [mtz] ⁻	389.7	3.62	-0.68
[EMIm] ⁺ [CNTz] ⁻	351.5	3.83	-0.77
[EMIm] ⁺ [NH ₂ tz] ⁻	399.8	2.94	-0.72
[EMIm] ⁺ [NO ₂ tz] ⁻	353.6	3.12	-0.78
[EMIm] ⁺ [NO ₂ Otz] ⁻	347.2	2.39	-0.82

The stability of compounds are also examined based on the energy gap (ΔE^*) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Conventional ILs (first two entries in Table 2) possess ΔE^* of ~5.5 eV while energetic ILs (EILs) are characterized with a lower band gap energy (2 – 4 eV). In general, a small ΔE^* helps the electrons to cross the band gap easily, leading to poor compound stability^{30,31} as this process destroys charge separation in the ion-pair. The derivatives of tetrazolate anions show good stability in terms of the predicted band gap. Among different derivatives of tetrazolate based EILs, ΔE^* predicts [EMIm]⁺[CNTz]⁻ as the most stable as it possesses the highest ΔE^* value 3.83 eV. The very high E_b (398.7 kJ/mol) obtained for [EMIm]⁺[trz]⁻ was decreased to 335.5 kJ/mol by dinitro substitution in the triazolate anion ([EMIm]⁺[dtrz]⁻). The electronic structural features have successfully been employed to tailor thermodynamic properties such as melting point of ILs. Generally, highly delocalised charge in the anion and shielded positive charge in the cation assist the formation of low melting ILs. In the given set of ion pairs, the best delocalization is observed for highly symmetric

anions like [dc]⁻ and [dtrz]⁻ as revealed from the MESP plot given in Fig. 2. There are many strategies reported to fluidize imidazolium based ionic liquids. Introducing weakly polar anions generally reduce the interaction energy between cations and anions resulting in reduced melting points and decreased viscosities.³² Another strategy is to introduce asymmetry into the imidazolium cation by using different substituents at the N1 and N3 positions.³³ Strong, directional and localized hydrogen bonds are also reported to enhance the fluid properties of imidazolium based ILs.³⁴

We have considered all these factors while designing the compounds and sought possible correlation between computed E_b and melting points of known compounds. Generally higher E_b correlates to higher melting point which suggest that the melting points of energetic ILs could be higher than the traditional ILs (first two entries in Table 2) and among them the [EMIm]⁺[NH₂tz]⁻ is expected to possess the highest melting point. Organic salts of [dc]⁻ anions, in general are known to possess relatively lower melting points³⁵ and reported melting point of [EMIm]⁺[dc]⁻ is -27 °C. Among the named EILs, [EMIm]⁺[CNTz]⁻, [EMIm]⁺[dn]⁻, [EMIm]⁺[dtrz]⁻, [EMIm]⁺[NO₂tz]⁻ and [EMIm]⁺[NO₂Otz]⁻ possess lower E_b than the [EMIm]⁺[dc]⁻ and indicate their existence in liquid state.

3.2 Thermochemical properties

It is important to determine the thermochemical properties of ILs in the vapor phase as the process of ignition and combustion take place in the gas phase. The thermochemical calculations using DFT methods (B3LYP, M06L, M05-2X, M06-2X) and ab initio method (G3MP2) are compared for compounds of known experimental heat of formation, $\Delta_f H^0$ in Table 3. Compared to the DFT methods, the G3MP2 results are very close to the experimental values. For the fourteen known compounds in Table 3, the error function Δq values are 20.6, 28.4, 48.7, 23.8 and 4.0 %, respectively observed for B3LYP, M06L, M05-2X, M06-2X and G3MP2 methods. The high accuracy of G3MP2 results is obvious from this data. Moreover, for the $\Delta_f H^0$ of hydrazine, two different experimental values are known and between them, the smaller value 90 kJ/mol which is closer to the high accuracy G3MP2 value 92.1 kJ/mol. Therefore, only G3MP2 data are used for calculating the propellant property of ILs.

Table 3. Experimentally reported $\Delta_f H^0$ (kJ/mol) values of known systems along with calculated DFT and ab initio values.

Compound	$\Delta_f H^0$ (kJ/mol)					
	DFT			ab initio	Experimental	
	B3LYP	M06L	M05-2X	M06-2X	G3MP2	
1,3-H-imidazolium cation	758.8	749.5	716.5	752.8	725.8	719.8 ³⁶
1,4-H-1,2,4-triazolium cation	867.0	869.3	908.1	877.7	847.3	836.0 ³⁷
Tetrazolate anion	192.4	202.4	222.4	228.3	186.1	200.2 ³⁷
1,2,4-triazolate anion	120.6	121.2	142.3	135.1	100.8	102.8 ³⁷
[BMIm] ⁺ [dc] ⁻	499.7	404.0	592.1	445.7	360.9	363.4 ¹⁸
[EMIm] ⁺ [dc] ⁻	510.3	422.2	576.8	466.4	404.1	391.7 ³⁸
Hydrazine	91.9	151.6	158.5	124.2	92.1	90.0 ³⁹ , 95.0 ⁴⁰
Monomethyl hydrazine	104.0	158.1	185.3	128.2	82.9	92.0 ³⁹
Pyridine	193.4	141.1	219.8	177.3	133.5	140.0 ⁴¹
Pyridazine	322.7	285.9	356.9	325.1	277.4	278.3 ⁴¹
Pyrazine	245.2	210.5	276.0	243.0	201.8	196.0 ⁴¹
1,2,3-triazine	435.9	411.5	455.6	477.4	403.3	416.0 ⁴¹
1,2,4-triazine	368.1	348.9	404.6	382.6	337.1	334.0 ⁴¹
1,3,5-triazine	256.8	239.8	282.9	263.4	226.4	226.0 ⁴¹

Table 4. The $\Delta_f H^\circ$, % (N + O) and Isp values of ion-pairs of ILs and hydrazine at G3MP2 level.

Compound	Molecular Formula	$\Delta_f H^\circ$ (kJ/mol)	(N+O) (Wt%)	Isp (s)	% HAN with IL for Isp = 263 s	Isp (s) maximum (% HAN)
Hydrazine	N ₂ H ₄	90.0	87.5	263	-	-
[EMIm] ⁺ [BF ₄] ⁻	C ₆ N ₂ H ₁₁ BF ₄	-1692.2	14.2	·	68	295 (80%)
[EMIm] ⁺ [PF ₆] ⁻	C ₆ N ₂ H ₁₁ PF ₆	-1909.2	10.8	105	63	287 (80%)
[EMIm] ⁺ [tz] ⁻	C ₇ N ₆ H ₁₂	441.9	46.7	221	54	317 (80%)
[EMIm] ⁺ [dc] ⁻	C ₈ N ₅ H ₁₁	401.3	39.5	208	58	314 (80%)
[EMIm] ⁺ [mtz] ⁻	C ₈ N ₆ H ₁₄	404.2	43.3	213	57	315 (80%)
[EMIm] ⁺ [trz] ⁻	C ₈ N ₅ H ₁₃	346.9	39.1	207	59	314 (80%)
[EMIm] ⁺ [dtrz] ⁻	C ₈ N ₇ H ₁₁ O ₄	305.9	60.2	241	34	315 (70%)
[EMIm] ⁺ [dn] ⁻	C ₈ N ₅ H ₁₁ O ₄	166.9	61.7	252	23	319 (70%)
[EMIm] ⁺ [CNTz] ⁻	C ₈ N ₇ H ₁₁	558.6	47.8	221	54	316 (80%)
[EMIm] ⁺ [NH ₂ tz] ⁻	C ₇ N ₇ H ₁₃	444.8	50.3	219	53	317 (80%)
[EMIm] ⁺ [NO ₂ tz] ⁻	C ₇ N ₇ H ₁₁ O ₂	418.8	57.7	239	40	315 (80%)
[EMIm] ⁺ [NO ₂ Otz] ⁻	C ₇ N ₇ H ₁₁ O ₃	387.1	60.6	246	33	316 (70%)
HAN	N ₂ H ₄ O ₄	-198.2	95.8	238	-	-

* A condensed species H₃BO₃ is formed.

For EILs to be used for propellant applications, they require high energy density which is often associated with large positive heat of formation. This in turn results in high combustion chamber temperature and hence a higher Isp. Conventional ILs, viz. [EMIm]⁺[BF₄]⁻ and [EMIm]⁺[PF₆]⁻ have negative heat of formation suggesting a lower energy content. The heat of formation increases from -1692.2 to +558.6 kJ/mol when the anionic part is substituted by energetic groups (Table 4). The computed $\Delta_f H^\circ$ of all the nitrogen rich energetic ILs possess much higher heat of formation than hydrazine and suggests their use for propellant applications. The highest value of $\Delta_f H^\circ$ (g) is obtained for CNTz (558.6 kJ/mol) derivative. The lower values of $\Delta_f H^\circ$ (g) for [EMIm]⁺[trz]⁻, [EMIm]⁺[Mtz]⁻ and [EMIm]⁺[dc]⁻ can be attributed to their higher carbon content.

Oxygen balance is another significant index of energetic materials which is a measure of oxygen deficiency or excess of oxygen in a compound required to convert all the carbon into carbon monoxide and all the hydrogen into water. Generally oxygen rich compounds have higher Isp as all elements gets converted to gaseous product resulting in increased thrust. In the present set of EILs, the absence oxygen content leads to relatively lower Isp for [EMIm]⁺[dc]⁻, [EMIm]⁺[NH₂]⁻, [EMIm]⁺[CNTz]⁻, [EMIm]⁺[tz]⁻, [EMIm]⁺[mtz]⁻ and [EMIm]⁺[trz]⁻ in spite of their higher values of $\Delta_f H^\circ$ (g) (> 400 kJ/mol). The highest Isp of 252 s is obtained for [EMIm]⁺[dn]⁻ with two N-NO₂ groups in the anion. In fact a linear correlation of Isp with total (N + O) weight % is observed for all the ILs studied in the present work (Fig. 3). The low oxygen balance of imidazolium based EILs can be overcome by using suitable oxidizer such as HAN and solvent properties of ILs can be beneficially exploited to form binary-monopropellant mixtures.⁴²

ILs has been tested for hypergolicity with HAN oxidizer and it showed no visible signs of reactivity at room temperature^{43,44}. Hence a monopropellant mixture of IL with varying percentage of HAN is analyzed using CEA, which would be thermally stable at room temperature and ignited thermally or catalytically. The Isp gradually increases with increase in the oxidizer concentration. This change is rapid in the 20 – 50 % concentration and reaches the peak region around 60 – 80 % concentration (ESI).

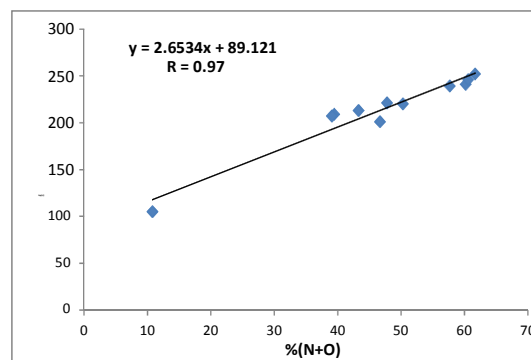


Fig. 3. Correlation graph between %wt of (N+O) and predicted Isp of [EMIm]⁺ ion pairs with 11 different anions given in Table 4.

These results clearly suggest that Isp tuning can be achieved by mixing ILs with suitable amount of HAN and these ILs may find use as fuel component in a binary propellant system. The ILs with oxygen rich anions, viz. [dn]⁻, [dtrz]⁻ and [NO₂Otz]⁻ attain the Isp of currently used propellant hydrazine (263 s) at 23 – 34% of HAN concentration (Table 4). An enhancement of 56 units in Isp is obtained for [EMIm]⁺[dn]⁻ for 70% HAN mixtures which provide the limit of Isp that can be achieved using the derivatives of imidazolium based ionic liquids (Table 4).

4. Conclusion

In summary, the quantum chemical computational studies accurately predict the thermochemistry of a variety of imidazolium based ILs. The high binding energy suggests ILs exist as ion-pairs in gaseous phase. The computed heats of formation of all the EILs of 1-ethyl-3-methylimidazolium cation and tetrazole derivatives, dicyanamide, triazole, dinitrotriazine, and dinitramine as anions are higher than that of hydrazine. ILs with a suitable oxidizer can be considered as a binary monopropellant due to ILs solvent properties. Among the 12 imidazolium based EILs studied, [EMIm]⁺[dtrz]⁻ and

[EMIm]⁺[dn]⁻, EMIm⁺[NO₂Otz]⁻ provide the best energetic performance in combination with HAN proposing the title compounds as potential green substitute for hydrazine. The Isp correlation with (N + O) content reveal the limit of Isp that can be achieved using imidazolium based ILs.

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Abbreviations

[EMIm] ⁺	1-ethyl-3-methylimidazolium cation
[BMIm] ⁺	1-butyl-3-methylimidazolium cation
Isp	specific impulse
DFT	density functional theory
EIL	energetic ionic liquid
[BF ₄] ⁻	tetrafluoroborate
[PF ₆] ⁻	hexafluorophosphate
[tz] ⁻	5-H-tetrazolate
[dc] ⁻	dicyanamide
[mtz] ⁻	5-methyl tetrazolate
[trz] ⁻	1,2,4-triazolate
[dtrz] ⁻	3,5-dinitro 1,2,4-triazolate
[dn] ⁻	dinitramine
[CNTz] ⁻	5-cyano tetrazolate
[NH ₂ tz] ⁻	5-amino tetrazolate
[NO ₂ tz] ⁻	5-nitro tetrazolate
[NO ₂ Otz] ⁻	5-nitro tetrazolate-2N-oxide
Δ _f H ⁰ (M,0K)	heat of formation of the molecule at 0K
CCSD(T)	coupled cluster method
Δq	normalized standard deviation
E _b	binding energy
ΔE [*]	energy gap between the HOMO and LUMO
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
MK charge	Merz Singh Kollman charge
HAN	hydroxyl ammonium nitrate

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