Investigation of Gelled Ionic Liquids as Hypergolic Fuels

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1 Abstract

The hypergolic reaction of 1-allyl-3-methylimidazolium dicyanamide (AMIM DCA), 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA) and 1-butyl-3-methyl-imidazolium dicyanamide (BMIM DCA) with nitric acid was investigated. AMIM DCA was characterized by thermal analysis (DSC, TGA) and density. Rheological measurements were performed on pure AMIM DCA and gelled AMIM DCA with silicon dioxide nanoparticles. The enthalpy of formation was calculated from the heat of combustion and the performance with nitric acid was calculated. The calculated results were compared to hypergolic agents such as monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH). The mass specific impulse of AMIM DCA is lower than MMH and UDMH. However, the volume specific impulse of AMIM DCA outranges the traditional hypergolic fuels. As an ionic liquid unlike conventional molecular liquids, it has practically no vapor pressure. Therefore significantly reduced environmental risk, better storage and handling properties are expected.

2 Introduction

Research and development of hypergolic systems has a long history because of the advantage of easy and reliable ignition and the possibility of repeatable thrust off and on turning “Schubabschaltung”. The first hypergolic system in service was hydrogen peroxide with a mixture of hydrazinhydrate, methanol and potassium tetracyanocuprate as a catalyst applied in the German rocket-powered fighter aircraft Me 163 [1]. Nowadays, hypergolic systems in use still consist of hydrazine and its derivates, such as unsymmetrical dimethylhydrazine (UDMH) and monomethylhydrazine (MMH).

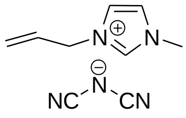
In the past 20 years, the US Army has developed gelled bipropellants and tactical missile propulsion systems that utilize hypergolic propellants for future combat systems [2]. Gelled propellants combine the advantages of solid propellants with these of liquid propellants. They are easy to handle and do not pour out on leakages like solid propellants and they are pumpable and burn well-defined in sprays like liquid propellants. One of the main problems preventing gelled hypergols from being fully applied in service is the environmental and health risk of the hydrazine and its derivates.

Although these systems are reliable and well investigated, the hazards and toxic nature of hydrazine and its derivates do not fulfill the requirements for current environmental demands. One alternative might be dicyanamide based ionic liquids. In literature imidazolium [3], triazolium [4] and 2,2-dialkyltriazanium [5] hypergolic systems are already reported. In this paper the environmental friendly hypergolic fuel 1-allyl-3-methylimidazolium dicyanamide (AMIM DCA) is presented and the hypergolic reaction with fuming nitric acid is investigated.

3 Results and discussion

As an ionic liquid AMIM DCA, unlike conventional molecular liquids, has practically no vapor phase. Therefore significantly reduced environmental risk, better storage and handling properties are expected. AMIM DCA shows a wide possible operational temperature range. The physicochemical properties are shown in Table 1. It is not sensitive to mechanical stimuli according to NATO STANAG 4487 and NATO STANAG 4489 procedures.

Table 1: Physicochemical properties and mechanical sensitivity data of AMIM DCA.

glass transition temperature		[°C]	- 94	
decomposition temperature	DSC onset	[°C]	207	
	TGA midpoint	[°C]	276	
density		[g/cm^3]	1.11	
impact sensitivity		[Nm]	> 50	
friction sensitivity		[N]	> 360	

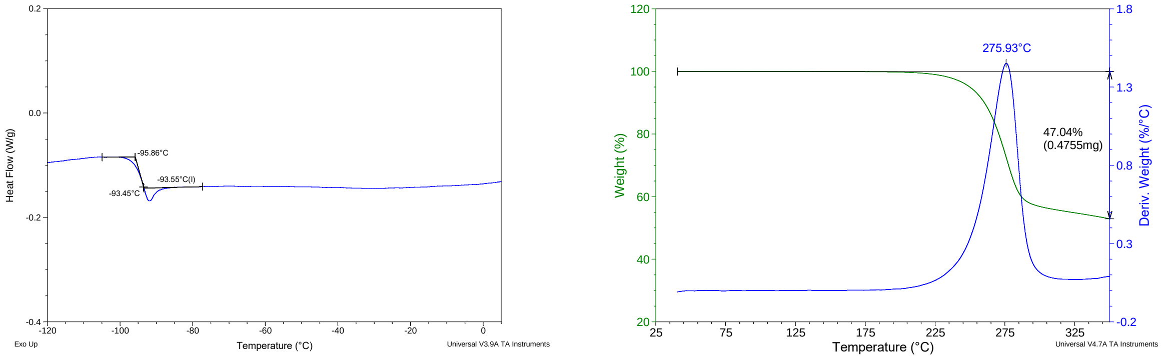


Figure 1: DSC with glass transition temperature and TGA of AMIM DCA.

To estimate the potential performance of AMIM DCA combustion measurements in a calorimetric bomb were done. The standard molar enthalpy of combustion ($\Delta_c H_m$) was calculated by using equation 2 with Δn_i (equation 3) as the total molar amount of gases in the products or reactants.

$$C_9H_{11}N_5 + 11.75\ O_2\ (g) \xrightarrow{\Delta n = -0.25} 9\ CO_2\ (g) + 5.5\ H_2O\ (l) + 2.5\ N_2\ (g) \quad (1)$$

$$\Delta_c H_m = \Delta_c U + \Delta nRT \quad (2)$$

$$\Delta n = \Delta n_i\ [\text{products (g)}] - \Delta n_i\ [\text{reactants (g)}] \quad (3)$$

$$\Delta_f H_m^{\circ} = 9\ \Delta_f H_m^{\circ}(CO_2) + 5.5\ \Delta_f H_m^{\circ}(H_2O) - \Delta_c H_m\ (C_9H_{10}N_5) \quad (4)$$

The standard enthalpy of formation ($\Delta_f H_m^{\circ}$) was calculated using Hess's Law and the standard values of heats of formation for water and carbon dioxide [6]. The formation of nitric acid was determined with ion chromatography and was considered in the calculations.

Table 2: Thermochemical properties of AMIM DCA.

oxygen balance	[%]	-196
$\Delta_c U$	[kJ/mol]	-5447
$\Delta_f H_m$	[kJ/mol]	+348 ± 5
heat of explosion[a]	[J/g]	2909

[a] calculated with ICT Code [7].

The important hypergolic fuels currently in use, compared to AMIM DCA are listed in Table 3. The glass transition temperature of AMIM DCA is significantly lower than the melting point of hydrazine and its derivates. However, due to the increasing viscosity at very low temperatures a usage down to the glass transition temperature is limited.

For applications at higher temperatures AMIM DCA is better than MMH, UDMH and hydrazine due to the absence of a boiling point at atmospheric pressure and a thermal stability up to 200 °C.

Table 3: Physical properties of hydrazine and its derivates compared to AMIM DCA.

substance	melting point [6]	boiling point [6]	enthalpy of formation [6]	vapor pressure at 25 °C [6]	density [7]
	[°C]	[°C]	[kJ/mol]	[kPa]	[g/cm^3]
MMH	-52	87	+54.18	6.3	0.874
UDMH	-57	64	+48.83	20.9	0.786
hydrazine	+1.54	113.5	+50.63	1.9	1.004
AMIM DCA		207(decomposition)	+348 ± 5	< 0.1	1.110

The synthesis [8] and hypergolicity [9] of AMIM DCA has been already reported with an ignition delay of 43 ms for 100% fuming nitric acid [9]. Hypergolic ignition tests performed at ICT (shown in Figure 2) revealed an ignition delay of (14 ± 6) ms. The realistic ignition delay might be even lower when determined with the two jet method [10] and using different inhibited nitric acid compositions, with and without ignition catalysts.

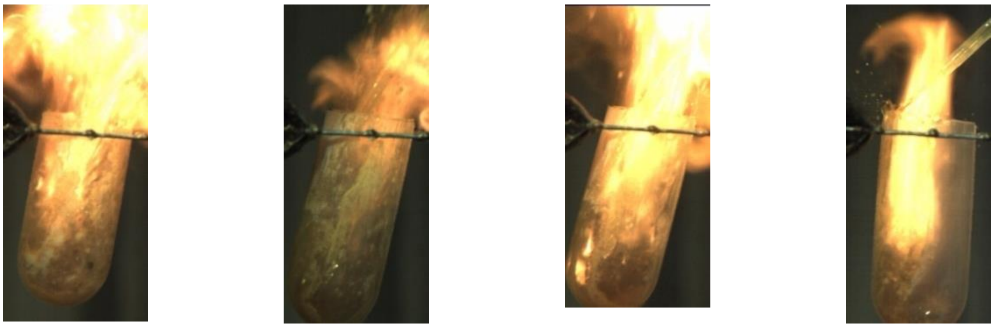


Figure 2: Pictures from high-speed videos from different test runs showing the hypergolic reaction of AMIM DCA with nitric acid.

The combustion temperature was measured from the hypergolic reaction of AMIM DCA with nitric acid by analyzing NIR emission spectra [11]. Temperatures above 2000 K were measured, which are in good correlation with the theoretical values.

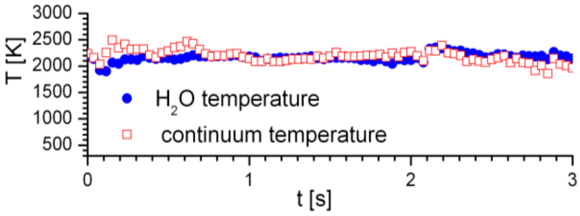


Figure 3: Temperature of the continuum emission and water bands in NIR from the hypergolic reaction of AMIM DCA with nitric acid.

The ignition mechanism of dicyanamide based substances and nitric acid has been already investigated by Chambreau et al. [12]. The suggested intermediate in the hypergolic reaction is dinitrobiuret with subsequent energetic decomposition shown in

Figure 4. Recently Litzinger et al. suggested additional reaction pathways. The additional reactions lead to the same overall reaction stoichiometry [13].

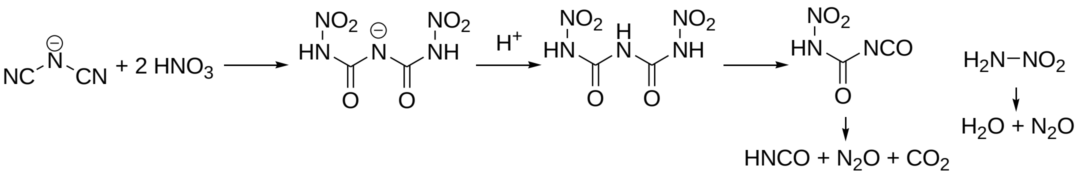
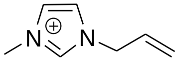
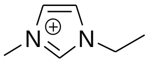
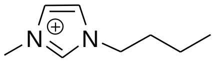


Figure 4: Suggested mechanism for the reaction of the dicyanamide anion with nitric acid after Cambreau et al. [12]

In order to investigate the influence of the allyl substituent in the hypergolic reaction EMIM DCA and BMIM DCA was used as a comparison (Table 4). The unsaturated substituent achieves a significant faster hypergolic reaction than saturated substituents like ethyl and butyl. Although the main step in the hypergolic ignition is the reaction of nitric acid with the dicyanamide anion, the ethylene group supports the hypergolic reaction due to its chemical reactivity.

Table 4: Ignition delay of dicyanamide based ionic liquids from the hypergolic reaction with nitric acid

cation	ignition delay [ms]
	14 ± 6
	27 ± 13
	60 ± 6

To evaluate the performance of AMIM DCA as a hypergolic fuel, the impulse was calculated using ICT Code [7] at an expansion ration of 70:1 and compared to MMH and UDMH. Pure hydrazine is not considered in the calculation due to the high freezing point which prevents practical usage in tactical missiles. The mass specific impulse and volume specific impulse in frozen state of hypergolic fuels with nitric acid is shown in Figure 5.

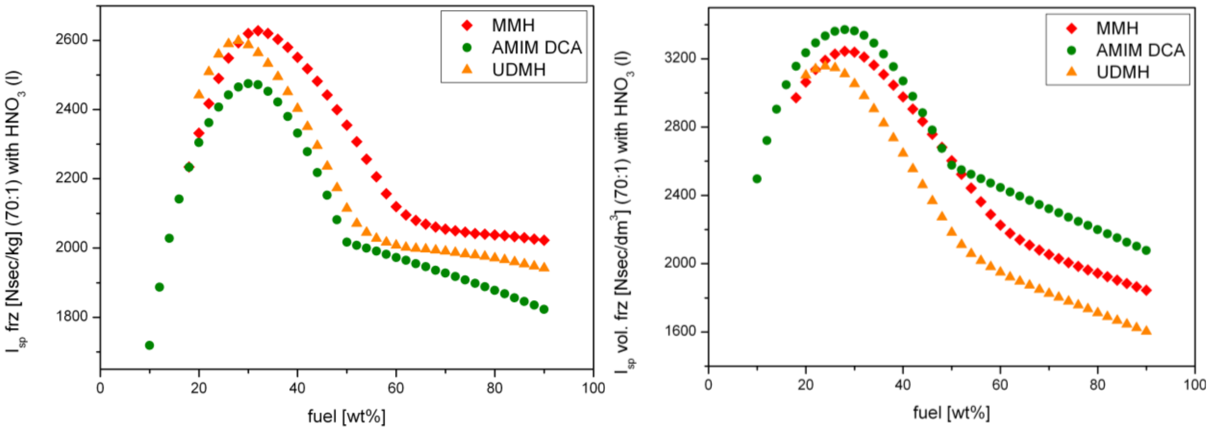


Figure 5: Mass specific and volume specific impulse (frozen equilibrium) of monomethylhydrazine (MMH), unsymmetrical dimethylhydrazine (UDMH) and 1-allyl-3-methylimidazolium dicyanamide (AMIM DCA) at an expansion ratio of 70:1.

In case of mass specific impulse, the hydrazine derivates achieve higher calculated values than the ionic liquid AMIM DCA. However, in case of volume specific impulse, AMIM DCA outranges the conventional hypergolic fuels. Subsequently, the IL is advantageous when small and powerful missiles are needed, like in tactical missiles with high volumetric specific impulse. By increasing the enthalpy of formation of the cation, the resulting ionic liquid achieves a greater specific impulse.

With regard to use AMIM DCA as propellant which requires pumping and atomization, the rheology was investigated in a temperature range of +100 °C to -60 °C. At 25 °C the pure AMIM DCA showed a viscosity of 24 mPas. By dispersion of silicon dioxide nanoparticles (6.5 wt%) in AMIM DCA a stable gel is formed and showed a typical shear thinning behavior at higher shear rates. The viscosity of the gelled AMIM DCA as a function of shear rate is shown in Figure 6.

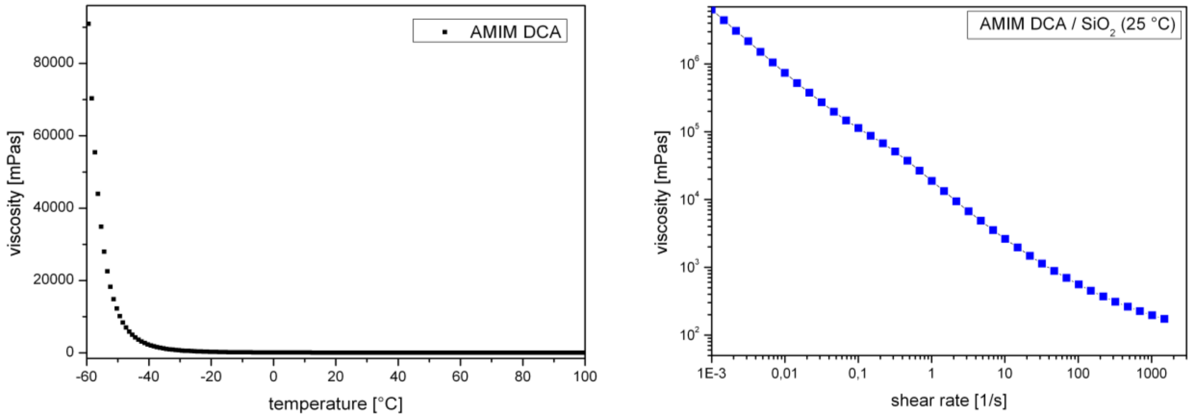


Figure 6: Viscosity of pure AMIM DCA between -60 °C and +100 °C (left) and gelled AMIM DCA with silicon dioxide as a function of shear rate at 25 °C (right).

4 Experimental

Differential scanning calorimetry (DSC) has been done by a TA instrument, Q 1000, using pierced aluminum pans. Scans were carried out on each sample at scan rates of 5 °C/min under argon flux. The reported values are onset temperatures. Glass transition points were measured from the 2nd heating cycle after cooling to -150 °C. Thermogravimetric analysis (TGA) has been done by a TA Q500 apparatus with a scan rate of 5 °C/min under nitrogen flux. Reported values are the central points according to DIN EN ISO 11358. Density was measured with a PYCNOMATIC ATC from Thermo Electron Corporation. For all calorimetric measurements, an IKA C 2000 system has been used. The calorimetric bomb was filled in each experiment with 5 mL water (HPLC purity) and, after each run, the combustion products were examined for unburned carbon. The combustion experiment was repeated four times. Nitric acid formation was determined by measuring the nitrate content in the water after each run. Reported values are the average of four measurements. Impact sensitivity and friction sensitivity tests were determined according to NATO STANAG 4487 and NATO STANAG 4489 procedures with the BAM drop hammer and friction sensitivity tester made by the former company Julius Peter (Berlin). Viscosity has been determined with a Physica MCR 501 from Anton Paar GmbH. 1-Allyl-3-methylimidazolium dicyanamide (AMIM DCA >98%), 1-ethyl-3-methylimidazolium dicyanamide (EMIM DCA >98%) and 1-butyl-3-methylimidazolium dicyanamide (BMIM DCA >98%) were purchased from IOLITEC and dried under HV and P_2O_5 for one week prior to use. Purity has been checked by elemental analysis with a Vario EL from Elementar for AMIM DCA $C_9H_{11}N_5$ (189.22) theo. C 57.13 H 5.86 N 37.01; found C 56.48 H 5.72 N 36.86. 100% fuming nitric acid was purchased from Merck and used as received.

The gel agents were nanometer sized silicon dioxide particles obtained from Evonik Industries AG, Frankfurt and had a density $\rho = 1.51$ g/cm^3 (determined by gas pycnometry) and a specific surface area $S_V = 260$ m^2/g (determined by gas adsorption). The mean size of the primary particles was 7 nm.

Hypergolic ignition tests were carried out using single-use cups for each test which have been filled with AMIM DCA. A high speed camera recording 3000 frames/s was used to determine the ignition delay times by counting the frames between the droplet first hitting the surface of the oxidizer and sign of the first ignition (Figure 2).

For temperature measurements, NIR-spectra were taken with a Plane Grating Spectrometer PGS-NIR 2.2 from Carl ZEISS GmbH. The wavelength of this monolithic miniature spectrograph ranges from 1 to 2.17 µm. Integration time varies from 100 µs to 1.6 s with a shortest interval of about 13 ms. A glass fiber is used as an optical entrance. The evaluation of NIR emission spectra uses the ICT-BaM code to model spectra of gaseous reaction products, soot and continuum radiation. The procedure is described in more detail in [11]. For the recent application, the water bands at 1.1 to 1.2 µm, 1.3 to 1.6 µm and 1.7 to 2.1 µm were evaluated. Continuum radiation was regarded as grey-body emission (Planck radiation with constant emissivity).

5 Conclusion

The hypergolic ionic liquids AMIM DCA, EMIM DCA and BMIM DCA were investigated in combination with nitric acid. The volume specific impulse of AMIM DCA outranges the traditional hypergolic fuels monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH) with nitric acid. Ionic liquids unlike conventional molecular liquids have practically no vapor pressure. Therefore significantly reduced environmental risk, better storage and handling properties are expected. With its wide temperature range of being liquid it will allow an increased operational temperature range, permitting new and powerful tactical missiles with storable hypergolic fuel.

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