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# Potential of ADN-based Ionic Liquid Propellant for Spacecraft Propulsion

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**Abstract**

As an alternative to hydrazine, ammonium dinitramide-based ionic liquid propellant (ADN-based ILP) was developed. It is mixture of the solid powders: ammonium dinitramide, monomethylamine nitrate, and Urea. It has a feature to be able to adjust the performance of monopropellant by change of the compositions because the constituents have different role: oxidizer, fuel, and freezing point depressant. By adjusting the components, it has high specific impulse and fuel rich and low freezing point comparing to hydrazine. The basic combustion characteristics of ADN-based ILP were investigated in the strand burner tests for application to thruster. The self-sustainable combustion, the linear burning rates, and the flame temperatures were shown in the results. The features of the ADN-based ILP were discussed on the basis of the results. As a problem of the thruster application, the ignition in vacuum was also discussed.


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*Keywords:* Ionic liquid; Monopropellant; Ammonium dinitramide; Strand burner; Spacecraft propulsion

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## 1. Introduction

Green and high performance monopropellants are required as replacements of hydrazine. As hydrazine is toxic, it will take costs to manufacture and operate spacecraft when the hydrazine was used as propellant. Because of this problem, the replacements have been studied such as the hydroxyl ammonium nitrate (HAN) based and the ammonium dinitramide (ADN) based solutions [1, 2].

As one of the replacements, JAXA and Japan Carlit Co., Ltd. developed solvent-free monopropellants, which contain ADN, monomethylammonium nitrate (MMAN), and Urea. Although these materials are solid at room temperature, the mixture of powders of them becomes liquid because of freezing point depression. These monopropellants are called as ADN-based ionic liquid propellants (ADN-based ILPs) in this paper. Ionic liquid (IL) is defined as salt whose freezing point is below 373K [3]. Thus, IL is liquid which contains only ions. The ADN-based ILPs are similar to IL in the point that they would be made of urea and ions of ADN and MMAN, which are salts with freezing points of 365 and 373-385K respectively. Therefore, the ADN-based ILPs would be low-volatility like ILs. It means to avoid sucking in them. By the way, some features of the ADN-based ILPs are remarked. Firstly, they are adjustable propellants in order to have three different role constituents: salts as oxidizer and fuel, and an additive for freezing point depression. Secondly, as mentioned in the next section, the ADN-based ILP at certain mass composition which is appropriately selected is a fuel-rich monopropellant. Therefore the exhausted gas conforms to materials especially such as thruster chamber and nozzle. Thirdly, in our consideration, the combustion efficiency might be higher than that of solution-type propellants because the components of the ADN-based ILPs would be thermally decomposed at the same time. Meanwhile volatile components from the solution surface such as alcohol and water would not be mixed in the same composition of original solutions for the different evaporation rates. In fact, the flame temperature of SHP163 which was HAN-based monopropellant was around 650 K lower than the adiabatic flame temperature in the strand burner tests [4].

Now some ILs have been believed to be non-flammable because of the non-volatility [5]. For the basic tests, Japan Carlit Co., Ltd. examined the ignition of the ADN-based ILPs in the atmosphere by fall of a droplet into a hot plate whose temperature was set. This test showed that the ADN-based ILPs can burn in atmosphere. The ignition temperatures were in the range of 473K-773K. In order to consider thruster application, however it is required to investigate the combustibility in the vacuum or inert atmosphere because the reaction with the oxygen in the air might cause the ignition in the tests.

The objective in this paper is to investigate the applicability of the ADN-based ILPs to thruster. Therefore, the best appropriate composition was selected for the thruster application. Then, the basic combustion characteristics were studied such as the combustibility and the self-sustainable combustion in the inert atmosphere and the pressure dependence of linear burning rate. Moreover, the high combustion efficiency was investigated by comparing the flame temperatures with the theoretical values.

In this work, strand burner test was selected for safety against the unknown propellant and obtaining the basic combustion characteristics. The strand burner test is classical experiment for investigating the dependences of linear burning rate on pressure or on composition or so on [6]. In this study, the pressure dependence of linear burning rate was measured and compared to that of the SHP163.

**Nomenclature**

| | |
|---|---|
| Isp | vacuum specific impulse |
| $T_{ad}$ | adiabatic flame temperature |
| $T_{ta}$ | time-averaged flame temperature |
| $T_f$ | freezing point of monopropellant |
| $\rho$ | density of monopropellant |
| P | pressure in the strand burner |
| r | linear burning rate |
| a | coefficient of linear burning rate in Vieille formula |
| n | pressure exponent in Vieille formula |

## 2. Selection of mass composition

Theoretical performances and properties of the ADN-based ILPs at each mass composition are showed in Table 1. In Table 1, the mass compositions are only listed at which the ADN-based ILPs can be liquid phase at room temperature. The mass compositions are arranged as the descending order of vacuum specific impulse. The vacuum specific impulse and the adiabatic flame temperature tend to increase with mass ratio of ADN increasing and mass ratio of Urea decreasing. The vacuum specific impulse of the ADN-based ILP at the mass composition 60/30/10 wt.% is 1.2 times higher than that of hydrazine and the density is 1.5 times as high as that of hydrazine.

The selection of appropriate mass composition of the ADN-based ILP is explained as follows. To begin with, the vacuum specific impulse should be higher than that of hydrazine. Secondly, maximum adiabatic flame temperature is limited by the material property of SiC/SiC for the radiative cooling chamber, around 1873K [7]. Thirdly, the propellant should be fuel rich monopropellant. According to the above conditions, there was only one appropriate mass composition 30/50/20 wt.%. The mass composition 30/50/20 wt.% was determined, although data were also obtained at the mass composition 40/40/20 wt.% taking account of the case that the temperature limit of the chamber will rise to around 1973 K in the future [8]. In the mass composition 30/50/20 wt.%, the ignition temperature was around 723K by the ignition tests of Japan Carlit Co., Ltd.

Table 1. Theoretical performances and properties of the ADN -based ionic liquids: The vacuum specific impulses Isp and the adiabatic flame temperatures $T_{ad}$ were calculated by NASA-CEA on the condition of chamber pressure 0.7MPa, expansion ratio 50, and frozen flow. The densities ρ were measured at 293K. The freezing points $T_f$ were measured by visual judgments of the phase conditions. The data of the densities and freezing points were provided by Japan Carlit Co., Ltd.

| A D N<br>wt.% | MMAN<br>wt.% | Urea<br>wt.% | Isp<br>s | $T_{ad}$<br>K | ρ<br>$g/cm^3$ | ρIsp<br>s $g/cm^3$ | $T_f$<br>K |
|---|---|---|---|---|---|---|---|
| 60 | 30 | 10 | 282 | 2631 | 1.50 | 423 | Around 283 |
| 40 | 50 | 10 | 269 | 2286 | 1.47 | 396 | Around 273 |
| 50 | 30 | 20 | 262 | 2214 | 1.49 | 390 | Around 273 |
| 40 | 40 | 20 | 250 | 1976 | 1.49 | 372 | Around 243 |
| 30 | 50 | 20 | 237 | 1743 | 1.45 | 343 | Around 243 |
| 30 | 40 | 30 | 213 | 1425 | 1.45 | 309 | Around 243 |

## 3. Experiments and Results

### *3.1. Experimental apparatus and conditions*

The strand burner test is explained as follows. In the experimental preparation, the ADN-based ILP (ADN/MMAN/Urea=30/50/20 wt.%) was poured until 25 mm height to a glass tube whose inner diameter was 10 mm. Some glass tubes have a 25 μm diameter R-Type (Pt and Pt-13%Rh) thermocouple in the position of 15 mm height from the bottom (Fig. 1 (a)). The glass tube was set to the strand burner (Fig. 1 (b)). The propellant was ignited by hot nichrome wire in the pressurized nitrogen gas. The pressure was controlled from 0.15 to 3 MPaA. The initial settings of pressure before ignitions are 0.15, 0.5, 1, 2 and 3 MPaA. The motion pictures at the time of combustion were recorded through the window of strand burner.

### *3.2. Self-sustainable combustions*

Table 2 shows the result of self-sustainable combustions at each setting pressure. The ADN-based ILP burned sustainably without heat source at many setting pressures except for 0.15 and 0.5 MPaA. At setting pressure 0.15 MPaA, the ADN-based ILP formed foam on the liquid surface and just decomposed but not burned. At setting pressure 0.5 MPaA, the ADN-based ILP burned after heating during around 50 seconds by hot nicrome wire. Soon after the heat supply was stopped, the flame vanished. In the case of setting pressure 3 MPaA, the pressure at the time of combustion was far from the setting pressure due to the higher pressure drop of nitrogen tank than that of

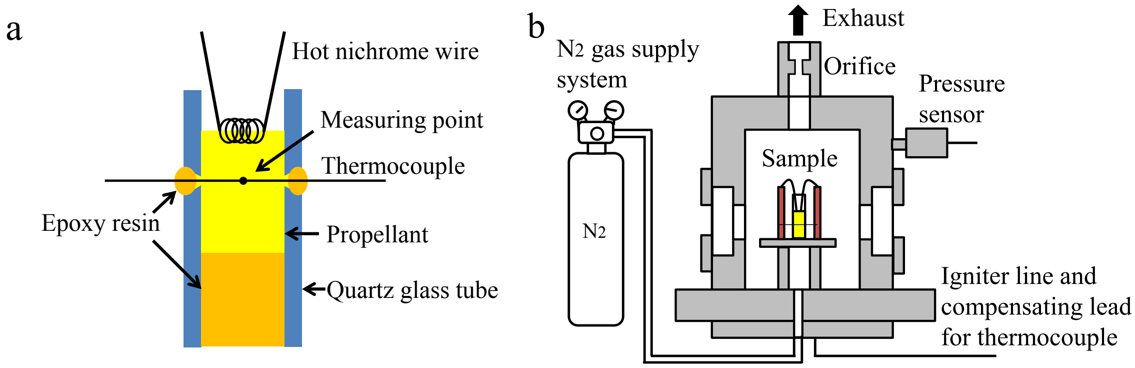


Fig. 1. (a) The cross-section of the glass tube which was filled with propellant; (b) The strand burner.

Table 2. Verification of self-sustainable combustion at setting pressure 0.15-3MPaA.

| Pressure settings | Pressure at the time of combustion | Self-sustainable combustion |
|---|---|---|
| MPaA | MPaA | - |
| 0.15 | - | No |
| 0.5 | 0.39 | No |
| 1 | 0.96 | Yes |
| 2 | 1.8 | Yes |
| 3 | 2.5 | Yes |

the other setting pressures. The pictures of the combustion were seen from the Fig. 2. The foams on the liquid surfaces were found at Fig. 2 (a), (b), (c). They might be the decomposition gas.

### *3.3. Linear burning rates*

Linear burning rates were measured by the motion pictures of the burning surface in the setting pressures 1, 2, 3 MPaA. The pressures at the time of combustion were calculated by the time-average. The pressures increased at the time of combustion as a part of exhaust gas remained in the strand burner. The pressure dependence of linear burning rate is showed in Fig. 3. It shows that the linear burning rates of the ADN-based ILP are higher than that of

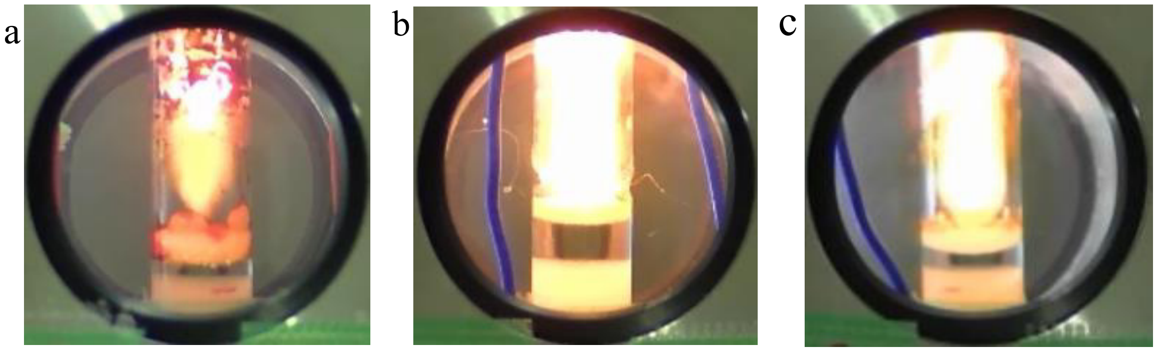


Fig. 2. Combustion waves of the ADN-based ionic liquid (ADN/MMAN/Urea=30/50/20 wt.%): (a) P=0.96 MPaA; (b) P=1.8 MPaA; (c) P=2.5 MPaA.

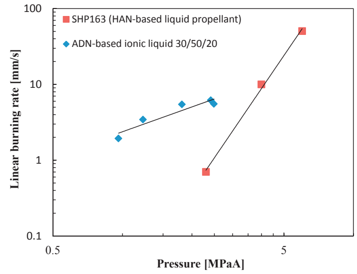


Fig. 3. Variation of the linear burning rates of ADN/MMAN/Urea mixture and SHP163 with pressure: SHP163 is HAN/AN /water/methanol monopropellant. The data of SHP163 were extracted from reference [4]. The solid lines are approximation curves of the Vieille formula (1).

SHP163 which is one of the prospective candidates studied in JAXA. According to approximation curves of the Vieille formula (1) which is well known relationship between linear burning rate r and pressure P, pressure exponents n of the ADN-based ILP and SHP163 are 1.1 and 4.5 respectively. The pressure exponent n of the ADN-based ILP is 0.24 times as large as that of SHP163.

$$r = aP^n \tag{1}$$

*3.4. Temperatures*

The temperature histories are showed in Fig. 4. The time-averaged flame temperatures $T_{ta}$ were calculated during the time when the temperatures were roughly constant. The flame temperatures at 1.2 and 1.8 MPaA were the almost same as adiabatic flame temperature 1743K, which was calculated by NASA-CEA at each pressure condition.

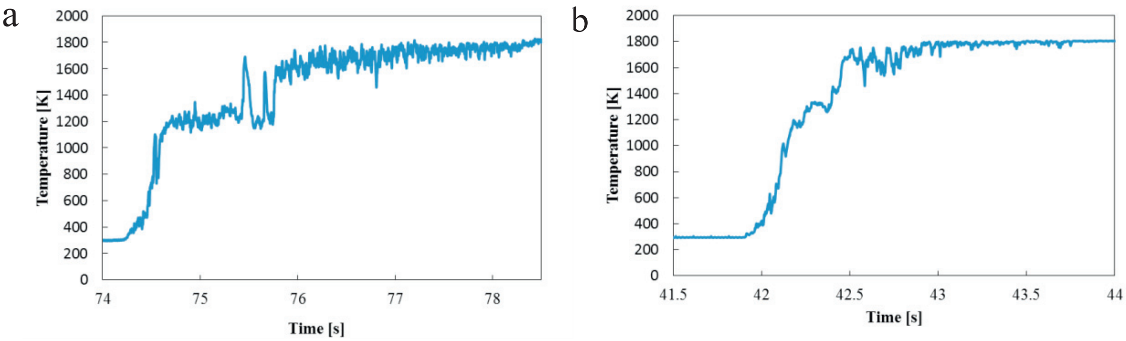


Fig. 4. Tempareture histories of combustion wave of the ADN-based ionic liquid (ADN/MMAN/Urea=30/50/20 wt. %), Tad=1743K: (a) P=1.2 MPaA, Tta=1707K; (b) P=1.8 MPaA, Tta=1792K: Tta denotes a time-averaged flame temperature.

## 4. Discussion and Conclusions

The applicability of the ADN-based ILP as monopropellant can be evaluated from the results. Some merits suitable to monopropellant can be seen as follows. Firstly, the composition was adjusted to be fuel rich for being compatible with the combustible materials. Secondly, the density specific impulse is around 1.5 times as large as that of hydrazine. Thirdly, the freezing point is around 243 K. Low freezing point enables the electric energy required for keeping it warm in space to decrease. Moreover, it can burn self-sustainably at more than at least 1 MPaA. This pressure level is around operating pressure in chamber of thruster. In addition, according to the flame temperatures in Fig. 4, the measuring flame temperatures were almost as same as the adiabatic flame temperatures. It means the almost complete combustions and increasing the practical performance of thruster. According to these results, the ADN-based ILP is superior monopropellant. On the other hand, there are some demerits as monopropellant. It has lower ignition limit during 0.39 to 0.96 MPaA, which is found in Table 2. In one side, it means the good point for safety in time to deal with. On the other side, it means difficulty to ignite the propellant in vacuum without catalyst. In fact, the ADN-based ILP could not burn and just decomposed at the pressure 0.15 MPaA. In the case of ignition by catalysts, it would be difficult to operate the thruster for a long time because the flame temperatures are larger than the temperature limit of catalyst support, around 1573 K [9, 10]. As another demerit, the pressure exponent of linear burning rate was lower than that of SHP163. It would means that pressure exponent of reaction rate was also lower than that of SHP163. It would be one of contribution to increase the ignition delay time.

In order to apply the ADN-based ILP to thruster, the ignition in vacuum is problem. In the case of the small thruster chamber, the decomposition gas of the ADN-based ILP might increase the chamber pressure until the lower ignition limit. On the other hand, in case of the large thruster chamber, it might be required to pressurize the chamber until the lower ignition limit by supplying external gas at the only time of ignition because the ADN-based ILP might be low-volatility like some ILs.

Nevertheless, the ADN-based ILP is attractive candidate for green propellant in the many points of the above performances. Especially, it is user-friendly propellant in the points of fuel rich monopropellant, high combustion efficiency, non-combustibility at ambient pressure, probably low-toxicity and low-volatility.

In conclusion, in order to investigate the applicability of the ADN-based ILPs to thruster, the appropriate composition was selected and the basic combustion characteristics were obtained. The ADN-based ILP at the appropriate composition 30/50/20 wt.% is fuel rich monopropellant. The density specific impulse is around 1.5 times as large as that of hydrazine. The result of the strand burner tests showed the combustibility of the ADN-based ILP in nitrogen atmosphere, existence of lower ignition limit during 0.39 to 0.96 MPaA, and the high combustion efficiency. The ADN-based ILP has superior performance and it is user-friendly propellant. However it would have a problem about ignition in vacuum because of existence of lower ignition limit and low-volatility. To improve this problem, pressurizing the chamber of thruster by external gas until lower ignition limit is one of the method for the application to thruster.

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