

Heat of Formation of ADN-Based Liquid Monopropellants

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Abstract: Energetic ionic liquids have obtained substantial attention the last decades as less toxic, or green, monopropellants to replace the carcinogenic and toxic hydrazine. Among the most promising hydrazine substitutes are propellants based on ammonium dinitramide, ADN, dissolved in a fuel/water mixture. These types of propellants are single phase mixtures, and thus their heats of formation are

influenced by the heats of solution and heats of mixing of the respective components used. These enthalpy contributions have been measured for three different ADN-based propellants (LMP-103S, FLP-106 and FLP-107) and their specific impulses have been calculated. The results show that ADN heat of solution must be considered in order to accurately calculate the specific impulse.

Keywords: Ammonium dinitramide · monopropellant · enthalpy

1 Introduction

Ionic liquid monopropellants are seen as promising green alternatives to replace the toxic and carcinogenic monopropellant hydrazine. An ionic liquid monopropellant can be prepared by dissolving an energetic oxidizer salt in a fuel/water mixture. The most studied oxidizer salts for this type of propellants are hydrazinium nitroformate (HNF) [1,2], hydroxyl-ammonium nitrate (HAN) [3,4], and ammonium dinitramide (ADN) [5,6]. High solubility is required to obtain a monopropellant with high performance and for that reason HAN and ADN are preferred. Some of the properties of these salts are shown in Table 1.

Liquid HAN-based monopropellants have been studied since the 1960s and were extensively studied in the 1980s for liquid gun propellants applications [10]. In the 1990s the interest for HAN-based liquid monopropellants for spacecraft propulsion increased due to the toxicity concerns of hydrazine [3,4,11,12]. The work on HAN-based monopropellant in the US have the last decade focused on the propellant AF-M315E, developed by the US Air Force Research Laboratory [13].

The development of liquid ADN propellants started at FOI in 1997 [5,14]. Methanol was one of the first fuels used but was shown to be incompatible with ADN. This could however be solved by increasing the pH by adding ammonia [15]. Since then, many fuels have been evaluated and formamides have shown to be of particular interest. *N*-methylformamide (monomethyl-formamide, MMF), and *N,N*-dimethylformamide, (DMF) were selected due to their ability to dissolve large amount of ADN, their low volatility (boiling point 200 and 153 °C respectively [16]), and good compatibility to ADN. The structure of MMF and DMF are shown in Figure 1.

In Table 2, the compositions of three different ADN-based monopropellants are shown. The composition of LMP-103S was selected to obtain an adiabatic combustion

Table 1. Properties of oxidizer salts considered for ionic liquid monopropellants.

Salt	Formula	Mw (g/mol)	Ω (%) ^a	S (%) ^b
HNF	N ₂ H ₅ C(NO ₂) ₃	183.1	+13	53 [7]
HAN	NH ₃ OHNO ₃	96.0	+33	95 [8]
ADN	NH ₄ N(NO ₂) ₂	124.1	+26	78 [9]

^a Oxygen balance. ^b Solubility in water at 20 °C.

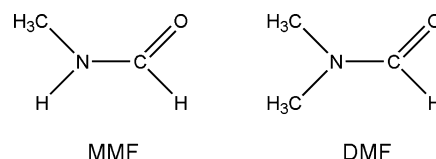


Figure 1. Structure of *N*-methylformamide (MMF), and *N,N*-dimethylformamide (DMF).

Table 2. Composition of ADN-based monopropellants.

LMP-103S	FLP-106	FLP-107
ADN 63.0 %	ADN 64.6 %	ADN 65.4 %
Methanol 18.4 %	MMF 11.5 %	DMF 9.3 %
Ammonia (aq) ^a 18.6 %	Water 23.9 %	Water 25.3 %

^a 25 % concentration.

temperature below 1600 °C, while FLP-106 and FLP-107 were optimised for maximum specific impulse by using the same procedure as described in [5,6].

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In order to accurately calculate the specific impulse and to evaluate the combustion efficiency, the heat of formation (ΔH_f) of the propellants must be known. Apart from the ΔH_f of respective components in the propellant, the heat of mixing (ΔH_{mix}), and the heat of solution (ΔH_{sol}) also influences the heat of formation of this type of propellants. The aim of this work was thus to thoroughly determine these enthalpy contributions and their influence on the specific impulse.

2 Experimental Section

2.1 Materials

The chemicals used in this work and respective supplier are shown in Table 3. All chemicals were used as received apart from ADN which was dried for two days at 40 °C prior to use. The water used was deionized using a Millipore Elix 3 Synergy.

Table 3. Chemicals used and respective supplier.

Chemical	CAS no.	Supplier and product
Ammonium dinitramide, ADN	140456-78-6	EURENCO, NSA 001 batch 20129009, > 99%
Ammonium nitrate, AN	6484-52-2	MERCK 101188, > 99%
Ammonia 25% (aq)	1336-21-6	MERCK Suprapur 1.05428, 25%
Dimethylformamide, DMF	68-12-2	Riedel-de Haën 33120, 99.5%
Methanol	67-56-1	MERCK SupraSolv 1.06011, 99.8%
Monomethylformamide, MMF	123-39-7	Aldrich 473936, 99%
KCl	7447-40-7	Sigma-Aldrich P9333, ≥ 99%

2.2 Methods

The MMF heat of combustion at constant volume (ΔU_c) was determined using an IKA C4000 adiabatic bomb calorimeter. The apparatus was calibrated using certified benzoic acid (IKA C723). In all cases the sample weight was approximately 1.3 g. 5 g water was placed in the bomb and nitric acid correction was performed according to DIN 51900 [17]. ΔU_c was calculated as,

$$\Delta U_c = (C_{cal}\Delta T - Q)/m_s \quad (1)$$

where, C_{cal} is the heat capacity of the calorimeter, Q is the sum of the contributions from the fuse, the ignition wire and the nitric acid formed, and m_s is the sample weight.

The heat of solution for ADN and AN in water were measured using a Dewar vessel equipped with a magnetic stirrer and a Testo 735–2 Pt100 precision thermometer. The amount of deionized water in the vessel was approximately 100 g and the sample weight approximately 1 g. The heat of solution was calculated according to equation 2,

$$\Delta H_{sol} = (C_{cal} + (m_{H_2O} + m_s)C_{p_{H_2O}})\Delta T/m_s \quad (2)$$

where the calorimetric constant (C_{cal}) was determined by using KCl ($\Delta H_{sol} = 235.86$ J/g) [18].

A ChemiSens Chemical Process Analyser CPA202 reaction calorimeter, equipped with a batch injector, was used to measure the heats of mixing and the heats of solution. The calorimeter conveniently enables determining the enthalpies directly, without measuring the heat capacity of the solutions. All measurements were performed at 25 °C.

3 Results and Discussion

In the literature, the heat of formation of ADN varies substantially from -162.8 kJ/mol [19] to -125.3 kJ/mol [20]. In [21] it was found that it exists a linear relationship between the heat of formation of nitrates and dinitramide salts having the same cation. Thus, if the heat of formation of a nitrate salt (XN) is known, the heat of formation of its corresponding dinitramide salt (XDN) can be estimated as,

$$\Delta H_f(XDN) = \Delta H_f(XN) + 230 n \quad (3)$$

where n is the number of anions per cation. Using the established data for the heat of formation for AN (-365.6 kJ/mol [16,22]), the heat of formation for ADN was estimated to be -135.6 kJ/mol. In [23] the heat of formation for ADN was thoroughly determined to be -134.6 ± 0.46 kJ/mol, which thus seems reasonable and is recommended for use.

Of the chemicals used in this work, the heat of formation for MMF in its standard state could not be found in the literature and was thus measured. The results from the bomb calorimeter experiments are shown in Table 4, where the heat of combustion at constant pressure was calculated as,

$$\Delta H_c(MMF) = \Delta U_c(MMF) + \Delta n R T \quad (4)$$

Table 4. MMF heat of combustion and heat of formation.

Sample	ΔU_c (J/g)	ΔH_c (kJ/mol)	ΔH_f (kJ/mol)
1	21259.6	1255.13	–246.4
2	21247.5	1254.42	–247.1
3	21220.1	1252.80	–248.7
Average ^a	21242 (20)	1254.1 (1.2)	–247.4 (1.2)

^a Standard deviation in parentheses.

Table 5. Heat of formation for chemicals used in the propellants.^a

Chemical	Formula	M_w (g/mol)	ΔH_f (kJ/mol)	ΔH_f (J/g)
ADN (cr)	$\text{NH}_4\text{N}(\text{NO}_2)_2$	124.056	−134.6 [23]	−1085
Ammonia (aq) ^b	NH_3	17.030	−81.1 [24]	−4762
DMF (l)	$(\text{CH}_3)_2\text{NCHO}$	73.094	−239.3 [16]	−3274
MMF (l)	CH_3HNCHO	59.068	−247.4	−4188
Methanol (l)	CH_3OH	32.042	−239.2 [16]	−7465
Water (l)	H_2O	18.015	−285.8 [16]	−15865

^a All data at their standard states except ammonia.^b NH_3 100 % (aq) at 298.15 K.**Table 6.** AN and ADN heat of solution in water.

Sample	ΔH_{sol} (kJ/mol) Measured	Average value	Literature value
AN (cr IV)	+25.20; +25.10	+25.15	+25.5 [25]
ADN (cr)	+35.83; +35.56	+35.70	+36.4 [23]

where Δn is the change in number of moles of gas during complete combustion, which for MMF is equal to −0.25. The MMF heat of formation was then calculated using equation 5,

$$\Delta H_f(\text{MMF}) = \Delta H_c(\text{MMF}) + 2\Delta H_f(\text{CO}_2) + \frac{5}{2}\Delta H_f(\text{H}_2\text{O}) \quad (5)$$

where $\Delta H_f(\text{CO}_2)$ and $\Delta H_f(\text{H}_2\text{O})$ are −393.5 and −285.8 kJ/mol, respectively [16].

In Table 5 the heat of formation of all chemicals used in the propellants are presented.

Table 7. Heat of formation of FLP-106.

	ΔH (J/g)	m (g)	$m \cdot \Delta H$ (kJ)
ΔH_f (Water)	−15865	239	−3792
ΔH_f (MMF)	−4188	115	−481.6
ΔH_{mix} (MMF in water)	−76.8		−8.83
ΔH_f (ADN)	−1085	646	−700.9
ΔH_{sol} (ADN in MMF/water)	+160.2		+103.5
Sum:		1000	−4880

When dissolving ADN in water the temperature decreases substantially due to its positive heat of solution, ΔH_{sol} , see Figure 2. The ADN ΔH_{sol} was determined to be +35.7 kJ/mol. The ΔH_{sol} of AN was measured for comparison. The results are shown in Table 6 along with literature values, showing good agreement. These values are however only valid for dilute water solutions, when the ions are fully dissociated.

To determine the heat of formation of FLP-106, the heat of mixing and heat of solution at relevant concentrations must be known. The heat of mixing between MMF and water for the mass ratio (11.5/23.9), given in Table 2, was measured five times and the average was found to be −76.8 J/g per gram of MMF, with a standard deviation of 1.7 J/g.

The heat of solution of ADN in MMF/water at the concentrations given in Table 2 was measured twice to be +160.2 ± 0.2 J/g, or +19.9 kJ/mol. The heat of formation of FLP-106 was then calculated by summarizing the enthalpies of the respective pure compounds, the heat of mixing and heat of solution, as shown in Table 7, and was found to be −4880 kJ/kg.

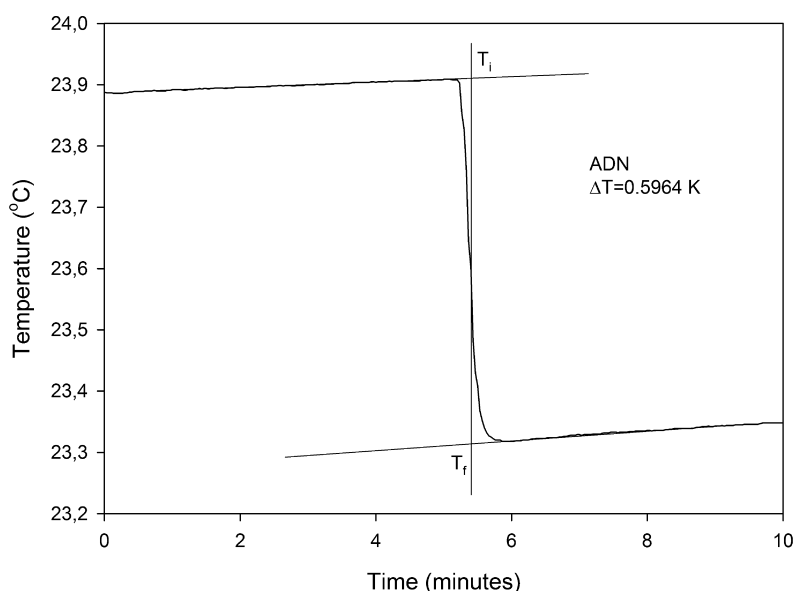
**Figure 2.** Typical ADN solubility thermogram (1 g ADN/100 g H_2O).

Table 8. Heat of formation of FLP-107.

	ΔH (J/g)	m (g)	$m \cdot \Delta H$ (kJ)
ΔH_f (Water)	−15865	253	−4014
ΔH_f (DMF)	−3274	93	−304.5
ΔH_{mix} (DMF/water)	−151.0		−14.0
ΔH_f (ADN)	−1085	654	−709.6
ΔH_{sol} (ADN in DMF/water)	+156.3		+102.2
Sum:		1000	−4940

The heat of formation of FLP-107 was determined using the same procedure as above. The heat of mixing between DMF and water for the mass ratio (9.3/25.3), given in Table 2, was measured four times and the average was found to be -151.0 J/g with a standard deviation of 3.1 J/g. The heat of solution of ADN in DMF/water, at the concentrations given in Table 2, was measured twice to be $+156.3 \pm 0.3$ J/g or 19.4 kJ/mol. The heat of formation of FLP-107 was calculated as shown in Table 8 and was found to be -4940 kJ/kg.

To calculate the heat of formation of LMP-103S, the heat of formation for aqueous ammonia at 25% concentration was first determined by fitting a second order polynomial to literature data shown in Figure 3, and was found to be -78.4 kJ/mol or -4604 J/g.

The heat of mixing between methanol and ammonia 25% *aq* for the mass ratio (18.4/18.6), given in Table 2, was measured twice and found to be -35.3 ± 0.7 J/g. The heat of solution of ADN in the methanol/ammonia/water mixture was also measured twice to $+141.9 \pm 0.7$ J/g, or 17.6 kJ/mol. The heat of formation of LMP-103S was calcu-

Table 9. Heat of formation of LMP-103S.

	ΔH (J/g)	m (g)	$m \cdot \Delta H$ (kJ)
ΔH_f (water)	−15865	139.5	−2213
ΔH_f (ammonia, <i>aq</i> 25 %)	−4604	46.5	−214.1
ΔH_f (methanol)	−7465	184	−1374
ΔH_{mix} (methanol/ NH_3 (<i>aq</i>))	−35.3		−6.5
ΔH_f (ADN)	−1085	630	−683.6
ΔH_{sol} (ADN in methanol/ NH_3 (<i>aq</i>))	+141.9		+89.4
Sum:		1000	−4402

Table 10. Sum formula for respective propellant.

Propellant	Sum formula	M_w (g/mol)
LMP-103S	$\text{CH}_{11.66}\text{N}_{4.01}\text{O}_{5.89}$	174.14
FLP-106	$\text{CH}_{14.66}\text{N}_{5.85}\text{O}_{9.26}$	256.82
FLP-107	$\text{CH}_{15.22}\text{N}_{5.86}\text{O}_{9.54}$	261.99

lated as shown in Table 9 and was found to be -4402 kJ/kg.

By calculating the sum formulas and the corresponding apparent molecular weights, the heats of formation in kJ/mol was calculated for respective propellant, see Table 10 and Table 11. The heats of formation, without taking ΔH_{mix} and ΔH_{sol} into account, are shown for comparison. In the latter cases, for LMP-103S, the calculations were performed using the heat of formation for ammonia (*aq*) shown in Table 5.

The theoretical vacuum specific impulse (I_{vac}) and the adiabatic combustion temperature (T_c) were calculated using the NASA CEA2 computer program [27,28] and the data in Table 10 and Table 11. An infinite area combustor with a

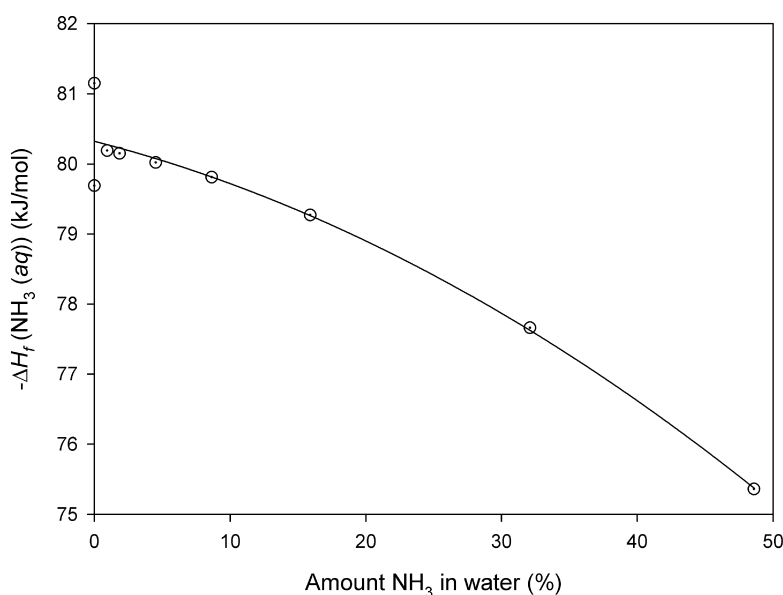


Figure 3. $\Delta H_f(\text{NH}_3(\text{aq}))$ as a function of concentration. Data from [24,26].

Table 11. Heat of formation for respective propellant.

Propellant	ΔH_f^a (kJ/kg)	ΔH_f^a (kJ/mol)	ΔH_f^b (kJ/mol)	ΔH_f^c (kJ/mol)
LMP-103S	−4402	−766.6	−766.7	−782.2
FLP-106	−4880	−1253	−1251	−1277
FLP-107	−4940	−1294	−1291	−1317

^a ΔH_{mix} and ΔH_{sol} considered.^b ΔH_{sol} considered.^c Neither ΔH_{mix} nor ΔH_{sol} considered.

chamber pressure of 2.0 MPa and a nozzle expansion ratio of 50 was used. Frozen composition was assumed during expansion. The results from the calculations are presented in Table 12 and show that the influence of the fuels heat of mixing on the specific impulse is low and can be neglected. The ADN heat of solution increases the specific impulse by approximately 3 s and the adiabatic combustion temperature by approximately 40 °C.

4 Conclusions

The ADN heat of solution is high (+36 kJ/mol) when fully dissociated in dilute water. When dissolved in respective fuel/water blend at relevant ADN concentration (~65 %), the ADN heat of solution is reduced to approximately +19 kJ/mol. By taking the ADN heat of solution into account, the calculated vacuum specific impulse increases in average by approximately 3 s and must thus be considered in order to accurately determine the performance. The influence of the fuels heats of mixing is low and can be neglected.

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Table 12. Calculated specific impulse and combustion temperature with and without considering the heat of mixing and the heat of solution. $p_c = 2.0$ MPa, $\epsilon = 50$.

ΔH_{mix} and ΔH_{sol} taken into account	LMP-103S		FLP-106		FLP-107	
	I_{vac} (s)	T_c (°C)	I_{vac} (s)	T_c (°C)	I_{vac} (s)	T_c (°C)
ΔH_{mix} ΔH_{sol}	254.5	1629	260.0	1900	261.1	1905
ΔH_{sol}	254.5	1629	260.2	1903	261.4	1909
Neither	251.5	1590	257.4	1861	258.6	1869

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