Research paper

Effects of amide compounds and nitrate salts on the melting point depression of ammonium dinitramide

Kento Shiota*[†], Masataka Itakura**, Yu-ichiro Izato**, Hiroki Matsunaga***, Hiroto Habu****, and Atsumi Miyake*****

*Graduate School of Environmental and Information Sciences, Yokohama National University and Japan Society for the Promotion of Science, 79−7 Tokiwadai, Hodogaya−ku, Yokohama-shi, Kanagawa, 240−8501 JAPAN
Phone: +81−45−339−3981

[†]Corresponding author: shiota−kento−jc@ynu.jp

**Graduate School of Environment and Information Sciences, Yokohama National University, 79−7 Tokiwadai, Hodogaya−ku, Yokohama−shi, Kanagawa, 240−8501 JAPAN

***Department of Chemical Engineering, Fukuoka University, 8−19−1 Nanakuma, Jonan−ku, Fukuoka−shi, Fukuoka, 814−0180 JAPAN

****Department of Space Flight Systems, Institute of Space and Astronautical Science (ISAS), Japan Aerospace Exploration Agency (JAXA), 3−1−1 Yoshinodai, Chuo−ku, Sagamihara−shi, Kanagawa, 252−5210 JAPAN

*****Institute of Advanced Sciences, Yokohama National University (YNU−IAS), 79−5 Tokiwadai, Hodogaya−ku, Yokohama−shi, Kanagawa, 240−8501 JAPAN

Abstract

Energetic ionic liquid propellants (EILPs) are expected to have applications in next-generation spacecraft propulsion, and ammonium dinitramide (ADN) is one of the most promising energetic materials for use in these propellants. The development of deep eutectic solvent systems, consisting of mixtures of two or more components, would allow the formulation of ADN-based EILPs that do not require traditional solvents. However, little is known regarding the effects of various additives on the melting point depression of ADN. In this study, the eutectic behaviors and melting points of small scale ADN mixtures with amide compounds or nitrate salts were investigated, using both visual inspection and differential scanning calorimetry (DSC). ADN/acetamide (AA) and ADN/monomethyl amine nitrate (MMAN) mixtures were found to be liquids at 60 °C, with the formation of a solid state at approximately 15 °C. Equimolar mixtures of ADN with AA, propionamide (PrA), MMAN and dimethyl amine nitrate (DMAN) each exhibited a eutectic point below 15 °C. The data show that equimolar mixing ratios are not ideal when formulating eutectic ADN compositions and that ADN-based EILPs have a tendency to supercool.

1. Introduction

Hydrazine is widely used as a monopropellant for spacecraft propulsion, even though it is toxic and has a high vapor pressure and thus requires special care during handling[1]−[3]. Less toxic monopropellants could lead to substantial cost savings, and a potential alternative is to use solutions of solid energetic materials. ADN and hydroxyl amine nitrate (HAN) are highly energetic materials with applications as next generation propellants[4]−[12]. For this reason, there have been many studies aimed at developing ADN or HAN-based liquid propellants, although issues remain regarding combustion problems associated with the use of solvents[13]−[20]. One approach to mitigating this problem is to use energetic

ionic liquids (EILs) as propellants. Ionic liquids (ILs) are salts that adopt a liquid state below 100 °C and are typically nonvolatile, with higher degrees of chemical and thermal stability compared to those of standard organic solvents[21)−22)]. In addition, the physical properties of ILs can be easily tuned by changing the component ions. Typical EIL cations include N-heteroaromatic compounds such as imidazolium, triazolium and tetrazolium ions and ammonia derivatives such as ammonium, iminium, triazanium and hydrazinium ions. Common EIL anions include azolates, dicyanamides, dinitramides, nitrocyanamides, nitrocyanomethanides, methanesulfonate, bis (trifluoromethylsulfonyl) imide, cyanoboronate, picrates, nitrates, perchlorates, azides, borohydrides, cyanoborates and metallic nitro complexes[23)−26)]. The EILs incorporating these cations and anions are synthesized by dissolving highly energetic materials such as azole and hydrazine derivatives in strong acids such as nitric, perchloric and dinitramidic acids. However, it is difficult to produce these substances on a large scale because of difficulties associated with purification and isolation of the product. For this reason, our own group has focused on deep eutectic solvents (DESs) as EILs for use in EILPs. DESs are liquids that are typically composed of two or more solid components capable of self-association, often through hydrogen bond interactions, such as between quaternary ammonium halide salts and hydrogen bond donors. These mixtures have lower melting points than those of the individual components in their pure form. EILPs are easier to prepare than other types of EILs, but exhibit similar physico-chemical properties to standard ILs[27)]. Studies of DESs have demonstrated that mixtures of choline chloride and urea (as the hydrogen bond donor) exhibit significant melting point depression. The molecular structures and properties have been studied using spectroscopy and theoretical analyses[28)−30)]. Eutectic mixtures consisting of energetic materials have also been reported, such as those based on ammonium nitrate (AN) with urea and AA or based on ADN[31)−34)]. Russell[35)] investigated a eutectic mixture of ADN and AN having a melting point of 55 °C at an ADN/AN molar ratio of 70/30. However, little is known about the effects of amide compounds and nitrate salts other than AN on the melting point depression or the eutectic properties of ADN. An improved understanding of the ADN eutectic mechanism would assist in the design of valuable EILPs with suitable physical properties and propulsion performance. The goal of the present study

was therefore to gain a better understanding of eutectic ADN systems by investigating the effects of amide compounds and nitrate salts containing amine cations on the melting point of ADN. This work involved the preparation of 200 mg scale equimolar ADN mixtures and the subsequent visual observation of these samples to assess the tendency of the resulting ionic liquids to supercool prior to crystallization. The melting of these equimolar ADN mixtures was also examined using DSC.

2. Experimental
2.1 Material

The ADN used in this work was obtained from the Hosoya Pyro-Engineering Co., Ltd. Japan. Urea (99%, Wako Pure Chemical Industries, Ltd., Japan), AA (98%, Wako Pure Chemical Industries, Ltd., Japan), PrA (98%, Alfa Aesar, USA) and butyramide (BtA, 98%, Wako Pure Chemical Industries, Ltd., Japan) were selected as amide compounds. AN (99%, Wako Pure Chemical Industries, Ltd., Japan), MMAN and dimethylamine nitrate (DMAN, 98.5%, Showa Chemical Co., Ltd., Japan) were used as the amine nitrates. MMAN was synthesized from a methylamine solution (40%, Wako Pure Chemical Industries, Ltd., Japan) and nitric acid (60%, Wako Pure Chemical Industries, Ltd., Japan). The molecular structures of the compounds mixed with ADN are shown in Figure 1.

2.2 Observations of the phase states of 200 mg scale ADN mixtures

In these trials, 200 mg samples composed of equimolar mixtures of powdered ADN with various other compounds were prepared in 1.5 mL glass vials, working in a glove box at 20% relative humidity (RH). These samples were subsequently heated in a constant-temperature oven at 60 °C for 24 hours and then held around 15 °C at 20% RH. The appearance of these samples was observed visually at each step.

2.3 Melting point depression of ADN by amide compounds and nitrate salts

The melting points of binary ADN mixtures were determined using a DSC apparatus (TA Instruments DSC Q200) calibrated for temperature and heat flow based on the melting of high-purity indium (99.99%) at a scanning rate of 10 °C min⁻¹. Prior to DSC trials, approximately 6 mg of each equimolar mixture was loaded into an open
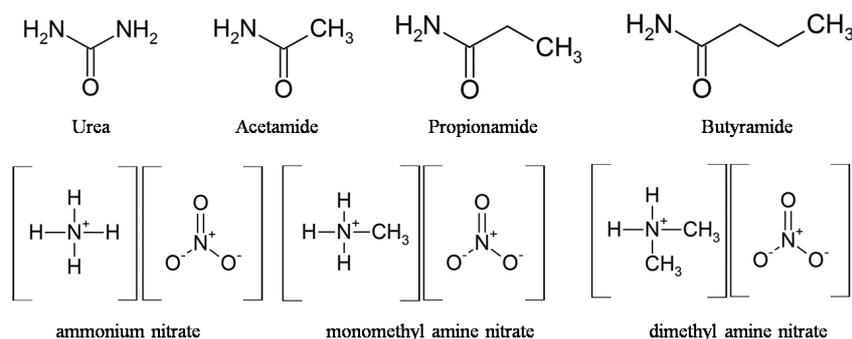
Figure 1 Molecular structures of the amide compounds and nitrate salts mixed with ADN.

aluminum container (ϕ 5 × 2.5 mm). Samples were heated and cooled in three steps with a concurrent 50 mL min^{-1} nitrogen flow. In the first step, each of the pure compounds was heated from 40 °C to its melting point at 10 °C min^{-1}. In the case of mixtures, each sample was heated from 40 to 90 °C or to the temperature at which the mass was reduced by 1%, based on preliminary thermogravimetric analysis at a heating rate of 10 °C min^{-1}. The mixture was then held at this temperature for five minutes to form a melt-mixed sample in the container. In the second step, each sample was cooled from the final temperature in the first step to −35 °C at 10 °C min^{-1}. To ensure freezing, the mixtures were held at −35 °C for 10 minutes. The third step consisted of heating from −35 to 90 °C at 2 °C min^{-1}. In the case of heating at 10 °C min^{-1} at the third step, exotherm derived from solidification of super cooling samples overlapped with endotherm derived from melting of the samples. Thus, heating at 2 °C min^{-1} was selected as heating rate at the third step. Melting of the mixture was determined from the endotherm onset temperature in this third step. When working with the pure compounds, a sealed aluminum pan (ϕ 6 × 4 mm) was used to inhibit sublimation prior to melting. The resulting data were used to establish a relationship between the melting point depression effects of additives on the ADN and the molecular volumes of the amide compounds or amine cations. The volumes were calculated using the FREE WHEEL Win software package, employing a calculation grid value of 200.

3. Results and discussion

3.1 Observations of phase states of 200 mg scale ADN mixtures

Observations showed that the AA or PrA mixed with ADN would melt at the contact interface immediately after mixing of the two compounds. Figure 2 presents the appearance of each mixture after mixing for one hour at room temperature around 15°C. The mixtures of ADN with Urea, BtA and AN are seen to have remained in the powder state, while the combinations containing AA, PrA, MMAN and DMAN partly formed a liquid phase at 15 °C. Figure 3 shows the samples after heating in an oven at 60 °C for 24 hours. The AA and MMAN mixtures are seen to be completely liquid. The Urea, PrA, BtA and DMAN mixtures have both liquid and solid portions, and the ADN /AN sample is essentially still in powder form. An equimolar mixing ratio of Urea, PrA, BtA, DMAN and AN mixtures is not composition ratio of eutectic because there are both liquid and solid phase at 60 °C, and eutectic temperature of ADN and AN mixture is 55 °C. The photographs in Figure 4 are of mixtures stored at 15 °C and 20% RH for 24 hours after the heat treatment. Interestingly, the ADN/AA mixture remained a liquid but solidified few days later, likely because a supercooled liquid was obtained after heat treatment. The ADN/ MMAN mixture formed needle-like crystals within the liquid phase after cooling around 15 °C for 24 hours. There were no liquid phase in the PrA, BtA and DMAN mixtures. Similarly to these mixtures, it is suggested that

Urea   AA   PrA   BtA   AN   MMAN   DMAN

Figure 2   States of ADN mixtures after powder mixing and then sat for one hour.

Urea   AA   PrA   BtA   AN   MMAN   DMAN
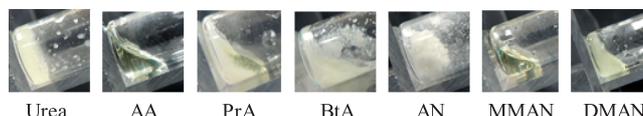
Figure 3   States of ADN mixtures after heating at 60 °C for 24 hours.

Urea   AA   PrA   BtA   AN   MMAN   DMAN
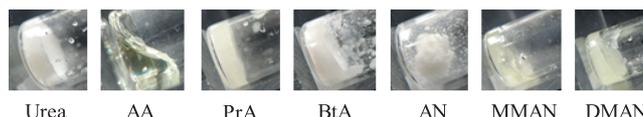
Figure 4   States of ADN mixtures after storage at 15 °C and 20% RH for 24 hours after heat treatment.

an equimolar mixing ratio of ADN with AA or MMAN mixture is not ideal when formulating eutectic compositions.

3.2 Melting point depression of ADN by amide compounds and nitrate salts

Figure 5 presents the DSC curves of ADN/amide mixtures as well as those of each individual substance during the third step of the trials. Figure 6 shows the DSC curves of ADN/amide mixtures. These data shown that the onset temperature of ADN melting was 92 °C, in good agreement with previous reports[33]. The ADN/Urea mixture exhibits a sharp endotherm along with a broader peak between 40 and 70 °C. The first endotherm is attributed to a eutectic point at 48 °C, while the broad endotherm is due to melting of the ADN and/or Urea. The ADN mixture with AA shows a significant endotherm at 9 °C (representing the eutectic point) and the baseline after the endotherm shifts upward at 65 °C as the solid state in the mixture melts completely. ADN and PrA specimen has an endotherm at 11 °C that is ascribed to melting of the mixture and a broad endotherm around 70 °C. Thus, both AA and PrA lowered the melting point of ADN to about the same extent. The sample containing ADN and BtA shows a eutectic point at 51 °C, and so BtA had approximately the same melting point depression effect as Urea. Overall, the ADN/AA mixture had the lowest melting point.

Figure 7 provides the DSC curves obtained from the ADN, nitrate salts and their mixtures. An endotherm appears in the ADN/AN mixture at 52 °C owing to the solid-state transition of AN along with a second endotherm at 57 °C due to melting of the mixture. The melting point is little higher than that reported from a previous study[35]. The eutectic points of the mixtures of ADN with MMAN and DMAN were 3 and 9 °C, respectively. Thus, the ADN/ MMAN mixture had the lowest melting point of the three nitrate salt mixtures under the current experimental conditions.
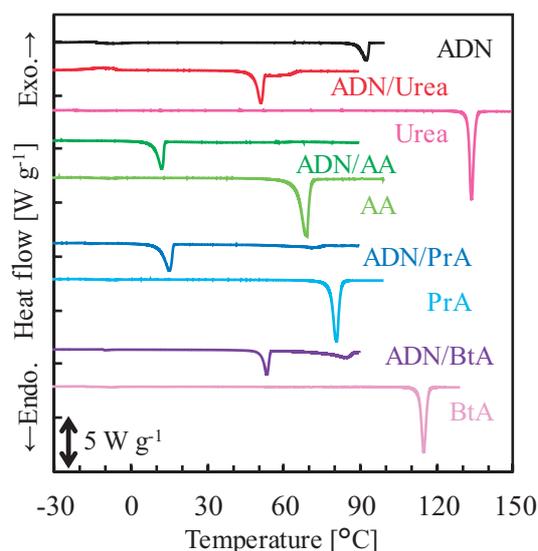
Figure 5 DSC curves obtained from ADN, amide compounds and their mixtures.
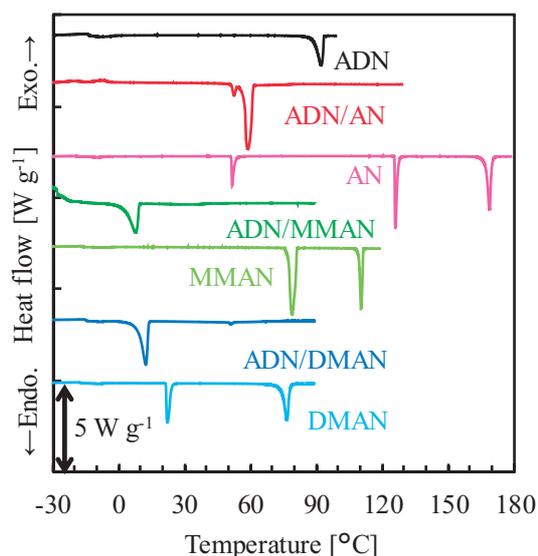
Figure 7 DSC curves obtained from ADN, nitrate salts and their mixtures.
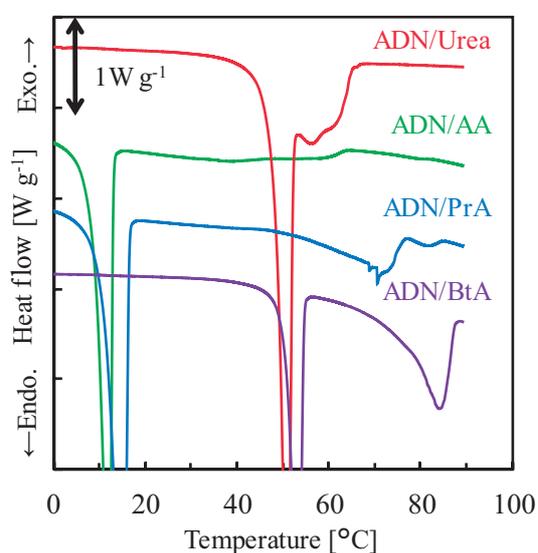
Figure 6 DSC curves obtained from ADN and amide compound mixtures.
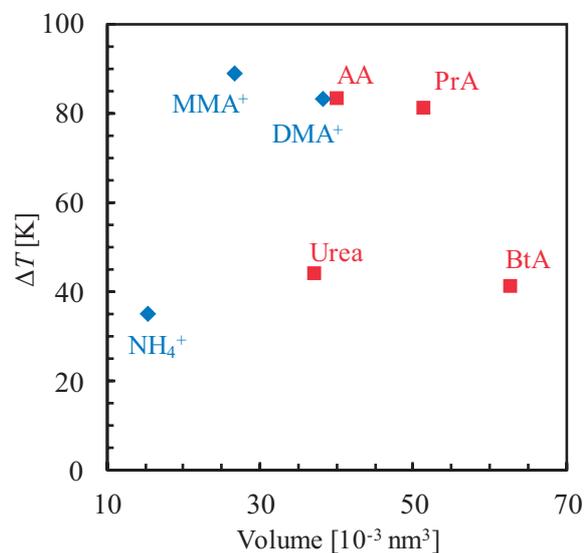
Figure 8 Relationship between ΔT and the molecular volumes of the additives.

Table 1 Absolute values of the melting point variation between that of pure ADN and those of mixtures (ΔT).

Additives	Urea	AA	PrA	BtA	AN	MMAN	DMAN
ΔT [ºC]	44	83	81	41	35	89	83

Table 1 summarizes the ΔT values, defined as the absolute values of the differences between the melting point of pure ADN and the eutectic points of the experimental mixtures under the present experimental conditions. The ADN/MMAN mixture had the lowest eutectic onset temperature of all samples. Figure 8 plots the relationship between ΔT and the molecular volumes of the amide compounds and amine cations. In the case of the amides except for Urea, the smaller molecule depressed the melting point of ADN to a greater extent. Abbott et al. proposed that increasing interactions between the anion and the hydrogen bond donor for choline chloride/urea system is a factor of the depression

in freezing temperature[28]. They indicated amides which are lower molecular weight have a tendency to depress in freezing point of choline chloride[36]. It is considered AA has stronger molecular interaction with ADN than PrA and BtA. Although Urea has a small molecular volume, it had a lesser effect than AA. This difference between Urea also and AA suggests that the methyl and the asymmetry of the molecular structure have an impact on the molecular interaction. Among the amine nitrates, the two nitrate salts except for ammonium ions lowered the melting point of ADN to a greater degree. It is believed that amine nitrates having methyl will exhibit a more pronounced melting point depression effect as well as

amides. It is likely that ion exchanges between ADN and amine nitrates except for AN occur, and there are multicomponent consists of ADN, amine nitrate, amine dinitramide and AN in liquid phase. The melting point of ADN and amine nitrates mixture except for AN have lower melting point than AN due to formation of the multicomponent.

4. Conclusion

This work assessed the effects of amide compounds and nitrate salts on the melting point of ADN. Observations of 200 mg scale ADN mixtures using visual observations and DSC were carried out to determine if complete melting of these mixtures occurred at equimolar ratios and whether the mixtures would undergo supercooling. The ADN/AA and ADN/MMAN mixtures were found to be in the liquid phase after heating at 60 °C for 24 hours. Solid phases formed in the ADN/MMAN mixture after cooling at 15 °C for 24 hours, while the ADN/AA mixture did not solidify until after several days, suggesting the formation of a supercooled liquid. These data are demonstrated that the optimum mixing ratio for eutectic compositions is not equimolar. From the DSC results, the eutectic points of AA, PrA, MMAN and DMAN mixtures with ADN are all below 15 °C. Thus, amides with short alkyl chains and nitrate salts except for ammonium ion evidently induce melting point depression in ADN.

Acknowledgement

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