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THERMAL HAZARD ANALYSIS OF MIXED SYSTEM OF HYDRAZINE AND NITRIC ACID

A. Miyake[1*], *A. Kimura*[1], *Y. Satoh*[2], *R. Shimizu*[2], *M. Inano*[2] *and T. Ogawa*[1]

[1]Department of Safety Engineering, Yokohama National University, Hodogaya-ku, Yokohama 240-8501, Japan
[2]Tokai Reprocessing Center, Japan Atomic Energy Agency, Muramatsu, Tokai, Ibaraki 319-1194, Japan

In order to obtain a better understanding of the thermal hazard of hydrazine and nitric acid mixtures which are used in plutonium and uranium recovery by extraction (PUREX) process during recycling of spent fuel in nuclear plant, DSC was carried out for the mixed system made by the small scale reaction calorimeter super-CRC in various conditions. It was found that the concentration of the nitric acid has a strong influence on the thermal behavior of the mixed system, and hydrazine nitrate which is formed in the reaction in the mixture was determined by DSC with FTIR analysis.

Keywords: *DSC, FTIR, hydrazine, hydrazine nitrate, mixing hazard, nitric acid*

Introduction

Chemical reaction hazards from exothermic reactions are one of the major hazards faced in the production of bulk and fine chemicals. In the absence of an understanding of these hazards, it is possible to develop conditions that lead to a thermal runaway reaction. Due to the severity of the risk involved in a thermal runaway reaction, a thorough understanding of the thermal risk of new processes is necessary [1, 2].

Also in the nuclear fuel reprocessing plant some events and accidents due to chemical reactions have been reported such as Savannah River or Tomsk-7 [3] and the demand of evaluation of chemical reactions has been increasing. The nuclear fuel reprocessing can be divided into two methods; the wet method and the dry method. Plutonium and uranium recovery by extraction (PUREX) method is the main current of wet reprocessing method in industrial scale. In this method the spent nuclear fuel is dissolved by nitric acid and extracted using tri-*n*-butyl phosphate ($C_{13}H_{27}PO_4$) as an organic solvent with *n*-dodecane ($C_{12}H_{26}$) as a diluent. In a purification process after separation nitrate solution of uranus ($U(NO_3)$) or hydroxylamine (NH_2OH) are used as a reducing agent with hydrazine (N_2H_4) as an inhibitor of decomposition of hydroxylamine or hydroxylamine nitrate. It is pointed out that this process has a hazard of thermal instability and runaway due to the mixing reaction of hydrazine with excess nitric acid [4, 5].

In the previous paper we reported the thermal hazard of hydrazine monohydrate ($N_2H_4{\cdot}H_2O$) and the mixing hazard of hydrazine monohydrate and nitric acid (HNO_3) were determined [6]. In this paper to obtain an understanding of the thermal hazard of mixed system of hydrazine monohydrate and nitric acid with various concentrations, DSC was carried out for the mixed system made by the small scale reaction calorimeter super-CRC in various conditions at 50°C. From the experimental results of DSC and FTIR analysis for the mixed system the thermal behavior of HH/NA mixtures was discussed.

Experimental

Materials

Materials used in this study were hydrazine monohydrate ($N_2H_4{\cdot}H_2O$; HH) and nitric acid (HNO_3; NA). Both were reagents from Wako Chemicals Co. Ltd., and were used without further purification and prepared as desired concentration with deionized water.

Methods

Mixing hazard of HH and NA with super-CRC

The isothermal mixing hazard of HH with nitric acid was investigated using a small scale reaction calorimeter super-CRC of Omnical Co. Ltd. [7]. Figure 1 shows a schematic diagram of super-CRC. In this series of test 1.0 g of HH was injected into the 16 mL glass vessel where excess amount of NA was stirred at 50°C. The mass and the concentration of NA were

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[*] Author for correspondence: atsumi@ynu.ac.jp

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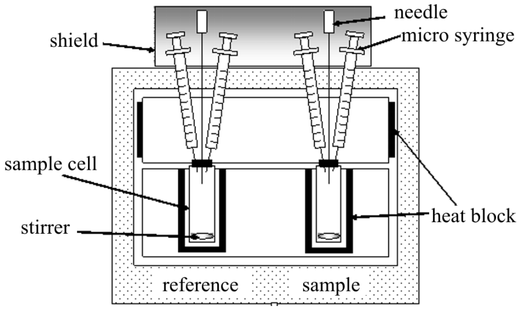

Fig. 1 Schematic diagram of reaction calorimeter super-CRC

varied as 9.0, 5.0, 1.0 g and 1.0, 3.0, 5.0 mol L^{-1}, respectively, and the temperature was kept at 50°C.

Thermal hazard of mixed system of HH/NA with DSC

To investigate the thermal behaviour of the mixed system of HH/NA the mixture which was taken from the residue of mixing experiment with super-CRC was cooled to room temperature and examined by pressure DSC 827^e of Mettler Toledo. 1.0 to 2.0 mg of the mixture was heated up to 400°C from room temperature at a heating rate of 10 K min^{-1}. The closed crucible made by the austenitic stainless steel (SUS303) specified in the JIS G 4303-4307 under 0.1 MPa air atmosphere [6].

Data analysis was performed using the software provided by Mettler Toledo and Ominical for respective instruments.

Results and discussion

Mixing hazard of HH and NA with super-CRC

As all the heat flow profiles were found as similar shape and it was considered that the reaction proceeded in the same manner. Table 1 shows heats of reaction of HH and NA in various conditions and the heat of reaction increased with the increase of the concentration of the nitric ion which reacted with HH in the mixtures [8, 9]. As the mixing hazard evaluation consists of the instantaneous hazard and hazard which is seen afterwards chemical analysis of the reaction products and the reaction scheme are needed for more detailed discussion. It was found that the concentration of NA and the mass of NA had a strong influence on the heat of reaction of HH and NA system and super-CRC is a useful tool to investigate the mixing hazard of the solution.

Table 1 Heat of reaction (J g^{-1}) of HH/NA system determined by super-CRC

HH/NA	NA		
	1 mol L^{-1}	3 mol L^{-1}	5 mol L^{-1}
1/1 g	146	200	266
1/5 g	283	560	916
1/9 g	398	779	1235

unit : Jg^{-1} hydrazine hydrate

Thermal hazard of mixed system of HH/NA with DSC

Figure 2 shows the influence of the concentration of NA on the thermal behavior of HH/NA mixtures which were mixed at 50°C. DSC curves of HH mixed with higher concentration (4 or 5 mol L^{-1}) of NA show sharp exothermic peaks at about 200°C after mild exotherm, and the thermal behaviour of them are different from those mixed with lower concentration NA. Table 2 shows the onset temperature and the heat of reaction of each mixture. The onset temperature of the first peak decreases and the heat of reaction increases with the increase of the NA concentration, and the onset temperature was not determined for the HH mixed with 1 mol L^{-1} NA.

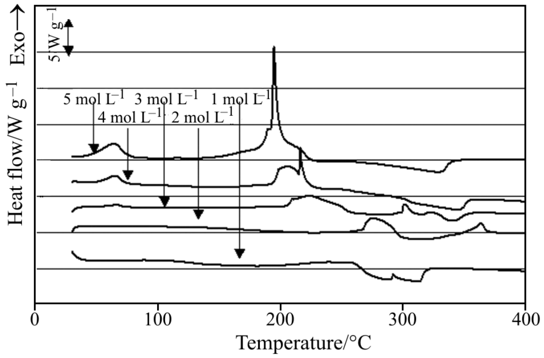

Fig. 2 Influence of NA concentration on DSC curves of HH/NA mixture

To investigate the thermal behaviour of mixed system of HH/NA in detail DSC curve of HH/NA (8 mol L^{-1}) is analyzed as shown in Fig. 3. Three exothermic peaks were observed in the DSC curve. Regarding the first peak (a), the onset temperature is about 100°C and the acidity of the reaction system was about 5 mol L^{-1}. The reaction of HH and NA of 5.4 mol L^{-1} at 100°C was confirmed to be NA and hydrazinium ion [9], the reaction is considered as following scheme.

Table 2 Influence of NA concentration on the thermal behaviour of NA/HH system

Concentration of NA/ mol L^{-1}	T_{onset}/ °C	Heat of reaction/ J g^{-1}
5	140	1046
4	170	492
3	181	516
2	252	259
1	–	232

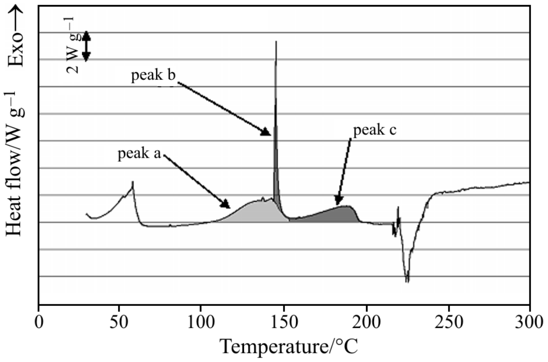

Fig. 3 DSC curve of mixed system of 8 mol L^{-1} NA/HH mixture

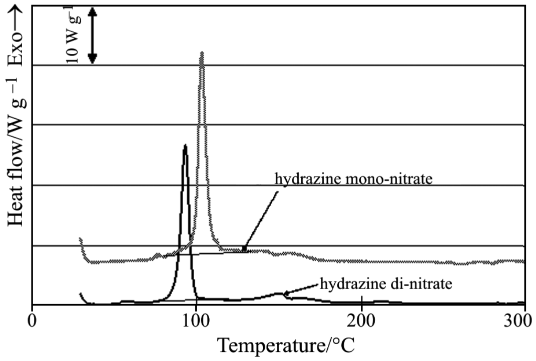

Fig. 4 DSC curves of hydrazine mono-nitrate and hydrazine di-nitrate

$$N_2H_5^+ + 0.8HNO_3 \rightarrow 0.19HN_3 + 0.17NH_4NO_3 + 0.7N_2 + 0.2N_2O + 1.8H_2O \quad (1)$$

The second peak (b) is the most violent and hazardous reaction which onset temperature is about 140°C, and it is thought to be a thermal decomposition of hydrazine nitrate (HN). HN is known for its explosive nature and is used as rocket propellant or energetic material. Figure 4 shows DSC curves of hydrazine mono-hydrate and hydrazine di-nitrate, which are prepared by the HH mixed with NA of 13 mol L^{-1} and separated by ethanol extraction [4]. Both curves show violent sharp peak at around 100°C, and the heat of reaction of hydrazine mono-hydrate and hydrazine di-nitrate are determined to be 2.7 and 2.1 kJ g^{-1}, respectively.

Figure 5 shows the FTIR spectra of white crystal of hydrazine di-nitrate with the KBr by JASCO FTIR 420 and of the mixture of HH and NA of 8 mol L^{-1}. Strong peaks were found at 1384, 1380 and 824 cm^{-1} which correspond to NO_3^-, and 1620 and 1627 cm^{-1} corresponding to NH_2. It is considered that HN exists in the mixed system of HH and NA of 8 mol L^{-1}.

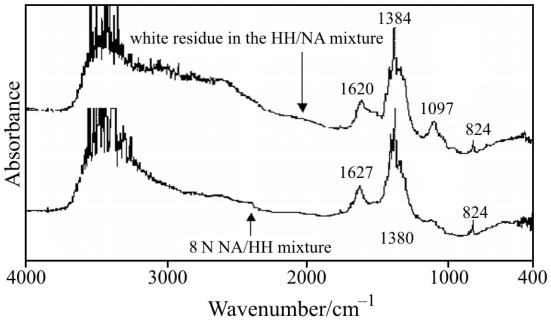

Fig. 5 IR spectra of white residue in the HH/NA mixture and 8 mol L^{-1} NA/HH mixture

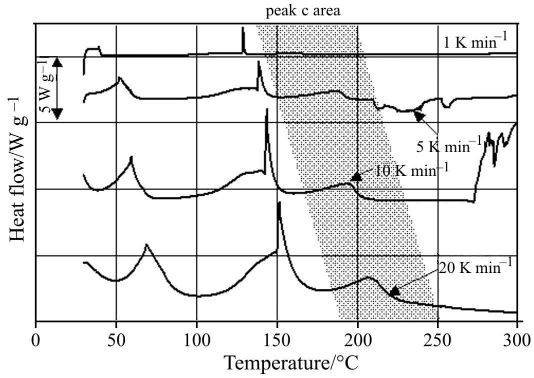

Fig. 6 Influence of heating rate on DSC curves of 8 mol L^{-1} NA/HH mixture

Figure 6 shows the influence of heating rate on the thermal behaviour of mixed system of HH and 8 mol L^{-1} NA. From the Kissinger plot analysis of the third peak (c) the apparent activation energy was determined to be 103 kJ mol^{-1}, which showed a good agreement of that of the thermal decomposition of HH [6].

Based on the experimental results the reaction mechanism of the mixed system of HH and NA is considered as follows.

When HH is mixed with NA with low acidity hydrazinium ion was formed. With the increase of the concentration of NA, i.e. the acidity of NA, HN is formed in the solution. When the concentration of the NA is high enough, such as 13 mol L^{-1}, HN is no more soluble and it educes as white crystal. It is concluded that the acidity, i.e. the proton concentration, has a strong influence on the HH and NA mixtures and HH when mixed with NA of higher concentration shows a violent reaction at around 140°C.

Conclusions

From the experimental investigation on the mixtures of HH and NA following conclusions can be drawn.

- From the calorimetric data the concentration of NA has a strong influence on the mixing heat of reaction of HH and NA system and super-CRC is a useful tool to investigate the mixing hazard of the solution.

- From the DSC results with the FTIR analysis the reaction mechanism was discussed. It was found that the proton concentration plays an important role in HH/NA system, and HN is formed when HH is mixed with the high concentration NA and the decomposition of HN shows a violent exothermic reaction.

Acknowledgements

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