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Thermal behaviour and phase diagram for the RDX/NQ binary system

Cui-Mei Yin *, Zi-Ru Liu, Yang-Hui Kong, Chao-Lin Jia, Xi-Mei Guo

Xian Modern Chemistry Research Institute, P.O. Box 18, Xian 710061, People's Republic of China

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Abstract

The phase diagram and thermal decomposition for binary mixtures of cyclotrimethylenetrinitramine (RDX) and nitroguanidine (NQ) were investigated by DSC and using a microscope with a heat stage (MHS). The eutectic compositions of the RDX/NQ binary system were obained by constructing a special phase diagram for the relation of the apparent fusion heat with the composition. The DSC results were confirmed by the phase diagram of liquidus temperature vs. composition constructed from MHS data.

Keywords: Binary system; DSC; Eutectic; Heat of fusion

1. Introduction

In order to improve combustion properties, energetic materials are generally added to propellants. It is important to study the thermal behaviour and solid–liquid equilibrium characteristics of these mixtures during combustion.

Cyclotrimethylenetrinitramine (RDX) and nitroguanidine (NQ) are key components for highly energetic propellants, and their thermal behaviour and solid–liquid equilibrium characteristics have an influence on the properties of the propellant.

In this work, differential scanning calorimetry (DSC) was used to study the thermal behaviour of the RDX/NQ binary system. The solid–liquid equilibria of the binary systems were investigated from the solidifying and liquifying points. Because RDX and NQ decompose near their melting points, it is impossible to measure the solid–liquid equilibrium and phase diagram from solidification data, and it was difficult to measure

* Corresponding author.

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the liquidus point of NQ in the mixture system. The melting peak of RDX on the DSC curve can be separated from its decomposition peak, but the liquidus point of RDX in the binary system is near its melting point. A microscope with a heat state (MHS) can be used to observe precisely the liquidus point in this binary system, only if the composition of the binary system is near the eutectic composition. Otherwise, the value measured is far from the practical liquifying line.

In this paper we propose a new method of measuring the composition of the eutectics by constructing the phase diagram of the binary system on the basis of the relation of the apparent heats of fusion and the compositions (HX-phase diagram). The method is not only useful in constructing the HX-phase diagram of the binary system, but is also suitable for investigating the solid–liquid phase equilibria of mixtures in which the components decompose on melting. In addition, the heat of fusion of materials which decompose on melting can be obtained by this method.

2. Phase diagram and calculation of eutectic composition

2.1. TX-*phase diagram of the binary system*

According to equilibrium thermodynamics, the liquidus temperature is related to the mole fraction of the solute component by

$$\ln X_i = \frac{\Delta_{\text{fus}} H_{ij}}{R}\left(\frac{1}{T_i} - \frac{1}{T_i^0}\right) \tag{1}$$

where X_i, $\Delta_{\text{fus}} H_{ij}$ and T_i are the mole fraction, the apparent heat of fusion and liquidus temperature of component i in the binary system, respectively; T_i^0 is melting point of the pure component i and R is the gas constant.

2.2. HX-*phase diagram of the binary system*

In order to construct the HX-phase diagram for the binary system on the basis of the relationship between the heat of fusion and the mole fraction of the component, it was confirmed that the heat of fusion is directly proportional to the mole fraction of the component and it is assumed that the eutectic is a mechanical mixture. Therefore, the apparent heat of fusion involves no heat of mixing and the temperature dependence of the heat of fusion is negligible.

When $X_i \geq X_i^0$ or $X_j \leq X_j^0$, where X_i and X_j, and X_i^0 and X_j^0 are the mole fractions of the component i and j in the binary system and in their eutectic, respectively, the apparent heat of fusion ΔH_1 of a eutectic in the binary system is

$$\Delta H_1 = K_1 X_j \tag{2}$$

where

$$K_1 = \Delta H_j + D \Delta H_i \tag{3}$$

and

$$D = X_i^0/X_j^0 \tag{4}$$

and the sum ΔH_1^0 of the apparent heat of fusion of the eutectic with that of the remainder of component i in the system is

$$\Delta H_1^0 = \Delta H_i + K_1^0 X_j \tag{5}$$

where

$$K_1^0 = \Delta H_j - \Delta H_i \tag{6}$$

and ΔH_i and ΔH_j are the heats of fusion of the pure components i and j, respectively.

When $X_i \leq X_i^0$ or $X_j \geq X_j^0$, the apparent heat of fusion ΔH_2 of a eutectic in the binary system is

$$\Delta H_2 = K_2 X_i \tag{7}$$

where

$$K_2 = \Delta H_i + \Delta H_j/D \tag{8}$$

and the sum ΔH_2^0 of the apparent heats of fusion is

$$\Delta H_2^0 = \Delta H_j + K_2^0 X_i \tag{9}$$

where

$$K_2^0 = \Delta H_i - \Delta H_j \tag{10}$$

It can be shown that the two lines obtained from Eqs. (2) or (5) and (7) have an intersecting point, whose coordinate on the composition axis corresponds to the eutectic component X_i^0 (or X_j^0). X_i^0 and X_j^0 could also be calculated from the D value, which is obained from the slopes and intercepts of Eqs. (2) or (5) and (7).

The use of these equations has been described elsewhere [1].

3. Experimental

3.1. Apparatus

The apparent heats of fusion and decomposition, and the melting and decomposition temperatures of the samples were determined using a Perkin-Elmer differential scanning calorimeter model DSC-2C. A microscope hot stage (model Boetius) was used to construct the temperature–composition (TX) phase diagram of the binary system.

3.2. Samples

The samples of RDX and NQ were ground in a mortar, and then mixed thoroughly.

4. Results and discussion

4.1. Thermal behaviour of the RDX/NQ binary system

The DSC curves for various mole ratios of the RDX/NQ binary system are shown in Fig. 1. The initial temperatures (T_{onset}), peak temperatures (T_m) and heats of fusion

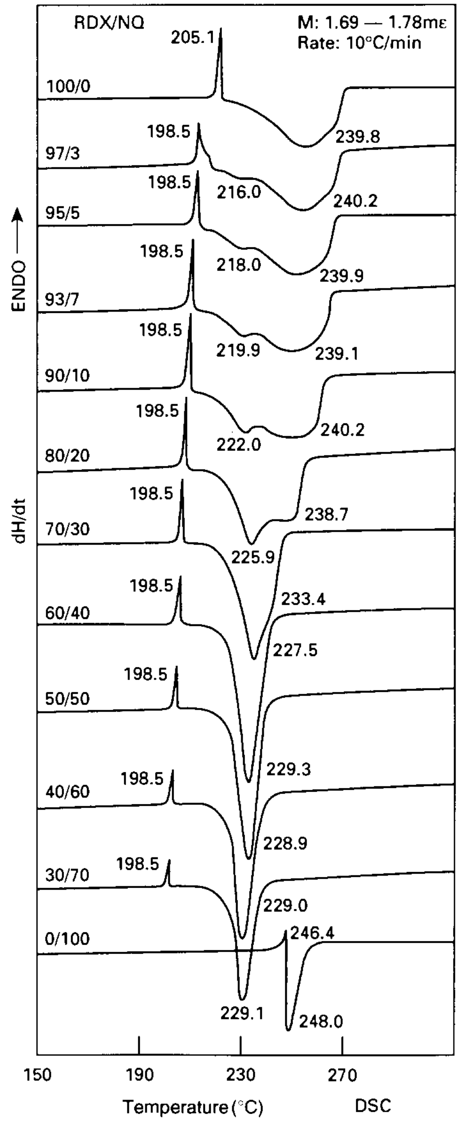

Fig. 1. DSC curves of RDX/NQ binary system.

($\Delta_{fus}H$) on melting or liquidus, the decomposition temperatures (T_{m1} and T_{m2}) and heats of decomposition ($\Delta_{dec}H$) are shown in Tables 1 and 2.

It is seen from Fig. 1 that the melting and decomposition processes of NQ cannot be separated by DSC, and strongly decomposing processes begin before the melting process is finished. Other experiments show that the size of the melting peaks of NQ

Table 1
The test results for the RDX/NQ mixture system by DSC

Mass fraction %	Melting		Decomposition		
	T_{onset}/°C	T_m/°C	T_{m1}/°C	T_{m2}/°C	$\Delta_{fus}H$/(J g^{-1})
100/0	203.7	205.1	–	239.8	2121.3
97/3	196.9	198.3	216.0	240.2	2077.8
95/5	197.1	198.8	218.0	239.9	2209.6
94/6	196.9	198.4	219.1	240.1	2205.0
93/7	197.0	198.6	219.9	239.1	2338.5
92/8	196.9	198.6	220.0	239.3	2466.8
90/10	197.1	198.6	222.0	240.2	2288.4
80/20	197.3	198.7	225.9	238.7	2409.3
70/30	196.8	198.2	227.5	233.4	2371.6
60/40	196.9	198.6	229.3	–	2254.7
50/50	196.5	198.1	228.9	–	2042.5
40/60	197.3	198.6	229.0	–	1788.2
30/70	196.7	198.1	229.1	–	1431.5
0/100	–	246.4	–	248.0	680.9

Table 2
The liquidus temperatures (by MHS) and the eutectic heat of fusion or the sum of heats of fusion of the eutectic and the remainder of the composition at melting (by DSC)

RDX/NQ		Liquidus temp./°C	$\Delta_{fus}H$/(kJ mol^{-1})
wt%	mol%		
100/0	100.00/0.00	205.1	33.43
97/3	93.81/6.19	204.0	33.69
95/5	89.91/10.09	201.5	33.74
94/6	88.02/11.98	199.5	34.09
93/7	86.17/13.83	199.5	34.37
92/8	84.26/15.64	202.5	32.96
90/10	80.84/19.16	204.7	31.96
80/20	65.23/34.77	207.5	25.11
70/30	52.25/47.75	210.5	20.39
60/40	41.29/58.71	215.5	15.73
50/50	31.92/68.08	219.0	11.87
40/60	23.82/76.18	–	8.70
30/70	16.16/83.84	–	6.00

decreases with decreasing heating rate [2]. When the heating rate is less than 2.5 K min^{-1}, the melting peak of NQ disappears. This shows that NQ is the material which is decomposing on melting.

The melting and decomposition temperatures of RDX are lower than those of NQ, but its melting can be clearly separated from its decomposition.

It can be seen that the DSC curves obtained with various mole fractions of RDX and NQ have endothermic melting peaks of constant temperature, which are lower than the melting peaks of RDX and NQ. This proves that the RDX/NQ binary system has a eutectic, the peak temperature of which is 198.5°C. Since the eutectic temperature is close to the melting temperature of pure RDX, the eutectic temperature cannot be separated from the melting temperature in the DSC curves in most cases. At a mass ratio of 97:3 (RDX/NQ), two endothermic peaks occur simultaneously in the DSC curve and are separable. At any other ratio of RDX/NQ, the melting peak of NQ could not be seen on the DSC curves because of the synchronization of melting and decomposition of NQ. Apparently, the decomposition of NQ occurs first because of the liquefication of the eutectic mixture or RDX, or because of the accelerating decomposition rate of liquifying NQ in the eutectic. Consequently, the exothermic peak of decomposition of RDX is overlapped with that of NQ. At a composition of NQ < 30 wt%, the first decomposition peak is that of NQ and at a composition of NQ > 30 wt%, the decomposition peak of NQ cannot be separated from that of RDX.

4.2. *The eutectic composition of the RDX/NQ binary system*

4.2.1. *Determination by DSC method*

When the content of NQ in the mixture system is greater than that of NQ in the eutectic composition, the liquidus peak of the remainder of the NQ in the mixture does not occur in the DSC curve; thus the endothermic peak area is equal to the heat of fusion of the eutectic and the heat of fusion is described by Eq. (7). When the content of NQ is less than that of NQ in the eutectic, i.e. that of RDX is greater than its eutectic composition, the liquidus peak of the remainder of the RDX cannot be separated from the eutectic peak. The endothermic peak area of fusion is equal to the sum of the fusion heat of RDX and that of the eutectic, and their fusion heats are described in Eq. (5).

Two straight lines were obtained by plotting the heats of fusion of the endothermic peaks against the mole fractions of the compositions of RDX and NQ, respectively, as shown in Fig. 2. These lines conform with Eqs. (7) and (5), respectively, and have an intersecting point whose coordinate on the axis of composition corresponds to the eutectic composition.

The slopes can be obtained from the two straight lines derived from Eqs. (8) and (6)

$$\Delta H_i + \Delta H_j/D = 39.38\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H_j - \Delta H_i = 4.32\ \mathrm{kJ\ mol^{-1}}$$

$$D = X_i^0/X_j^0$$

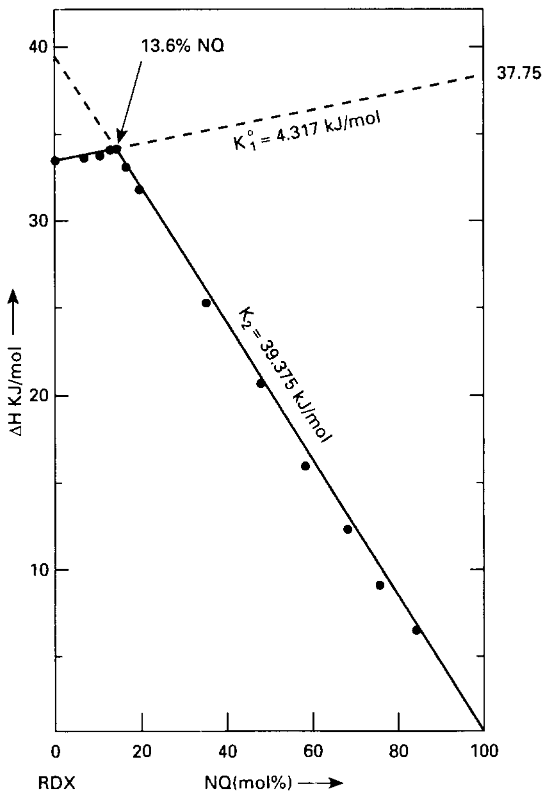

Fig. 2. HX-phase diagram for RDX/NQ binary system.

where ΔH_i and ΔH_j are the heats of fusion of pure RDX and NQ, respectively; ΔH_i was found from DSC, see Table 2. X_i^0 and X_j^0 are the mole fractions of RDX and NQ in the eutectic, respectively.

The eutectic compositions were calculated from the above three formulae, as shown in Table 3.

The heat of fusion of NQ obtained from the above formulae was 37.75 kJ mol^{-1}. The heat of fusion cannot be obtained in the normal way because of the synchronous melting and decomposition of NQ. Therefore, another advantage of this method is that heats of fusion of materials with simultaneous melting and decomposition can be determined.

4.2.2. Determination by MHS method

Table 2 shows the liquidus temperatures found by the MHS method at various mole fractions of the RDX/NQ binary system. Eqs. (11) and (12) were obtained from the data in Table 2 and on the basis of Eq. (1)

$$\ln X_i = 11.35 - 5431/T \quad (11)$$

$$\ln X_j = 19.76 - 10266/T \quad (12)$$

Table 3
Eutectic compositions of RDX/NQ

		DSC	MHS
mol%	NQ	13.60	13.77
	RDX	86.40	86.23
wt%	NQ	6.88	6.97
	RDX	93.12	93.03

where X_i and X_j are the mole fractions of RDX and NQ in the system, respectively.

The *TX*-phase diagram of the RDX/NQ binary system was constructed by using Eqs. (11) and (12) (see Fig. 3) to obtain the eutectic temperature of 198.5°C and compositions shown in Table 3.

By subtracting Eq. (12) from Eq. (11) and putting $T = T_e$ (the eutectic temperature of 198.5°C found from DSC), the eutectic composition can also be obtained (see Table 3).

4.3. *A comparison between the DSC and MHS methods*

The NQ eutectic compositions found in the binary system from both DSC and MHS are in good agreement, both being 6.9 wt%.

It can be seen from Fig. 3 that the liquidus point measured by MHS is much lower than the liquidus line when the content of NQ in the binary system is much more than that of NQ in the eutectic system.

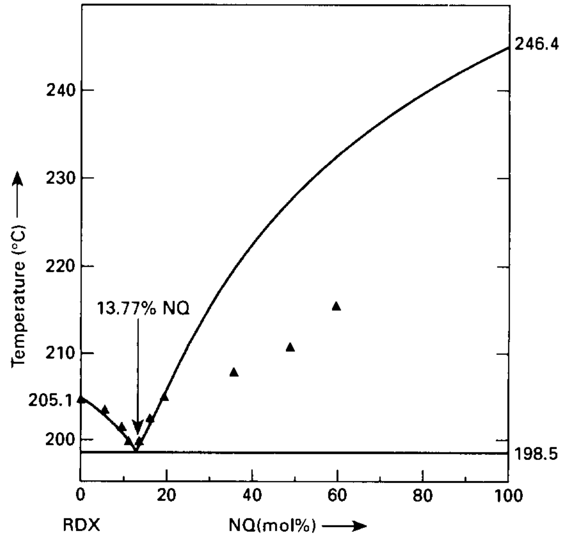

Fig. 3. *TX*-phase diagram for RDX/NQ binary system.

The higher the liquidus temperature, the more decomposition of NQ occurs, and the further away from the liquidus line it is. The heat of fusion of the eutectic of the binary system measured by DSC has a linear relationship with the NQ content. The heat of fusion is slightly lower because the decomposition of NQ begins before melting. The greater the particle size of NQ, the more apparent this becomes. This has been described in a previous article [2].

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