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Measurement of the eutectic composition and temperature of energetic materials. Part 1. The phase diagram of binary systems

Zi-Ru Liu *, Ying-Hui Shao, Cui-Mei Yin, Yang-Hui Kong

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

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Abstract

The eutectic compositions of eleven mixture systems (in three types) of energetic materials, including Tetryl/PETN, PETN/RDX, HMX/P Explosive and RDX/NQ, were obtained by constructing a special phase diagram for the correlation of the apparent fusion heat with the composition (HX-phase diagram). The apparent fusion heats of the systems and its eutectics as well as the eutectic temperatures were determined by differential scanning calorimetry (DSC). The results obtained from DSC were confirmed by TX-phase diagrams constructed from microscope heat stage method for these mixture systems.

Keywords: Binary system; DSC; Energetic material; Eutectic

1. Introduction

The cosolidification mixtures of energetic materials include intermolecular explosives (IMX), which are the most widely used class [1–3]. They have been prepared by constructing phase diagrams for their compositions to obtain the eutectics compositions [2–6]. Although many techniques for the construction of phase diagrams have been described in the literature [7–13], the operation is more difficult for some energetic materials owing to the lack of essential thermodynamic date and to thermal decomposition at or near their melting point.

* Corresponding author.

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In this work, an attempt was made to determine the eutectic compositions of the energetic materials by constructing a special phase diagram of the apparent fusion heat against composition, i.e. an HX-phase diagram. Differential scanning calorimetry (DSC) provided a fast, sensitive and accurate enough way of determining the apparent fusion heat and temperature of the eutectic. The eutectic compositions and temperatures of binary systems for three types of energetic material mixtures can be determined by this method. Ternary systems will be described in our next paper.

2. Principle of the method

In order to construct HX-phase diagrams of binary and ternary systems, it was assumed that the eutectic is a mechanical mixture, that its apparent fusion heat (ΔH) involves no heat of mixing, and that the temperature dependence of ΔH is negligible. ΔH will then be given by the relationship

$$\Delta H = \Sigma X_i^0 \Delta H_i \tag{1}$$

where X_i^0 is the mole fraction of component i in the eutectic, and ΔH_i is the apparent fusion heat of the pure component i in J mol^{-1}.

The HX-phase diagram of the binary system obtained on the basis of Eq. (1) is shown in Fig. 1.

If $X_i \leq X_i^0$ or $X_j \geq X_j^0$, where X_i and X_j and X_i^0 and X_j^0 are the mole fractions of the components i and j in the binary system and in the eutectic, respectively, we have

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

where

$$K_1 = \Delta H_i + \Delta H_j X_j^0 / X_i^0$$

When $X_i \geq X_i^0$ or $X_j \leq X_j^0$, we have

$$\Delta H_2 = K_2 X_j \tag{3}$$

where

$$K_2 = \Delta H_j + \Delta H_i X_i^0 / X_j^0$$

and the total apparent fusion heat of the system is

$$\Delta H_3 = \Delta H_j + (\Delta H_i - \Delta H_j) X_i \tag{4}$$

or

$$\Delta H_3 = \Delta H_i + (\Delta H_j - \Delta H_i) X_j \tag{4'}$$

It will be confirmed that the three lines obtained from the linear equations (2), (3) and (4) have a point of intersection P, whose coordinate on the X axis corresponds to the eutectic composition X_i^0 (or X_j^0).

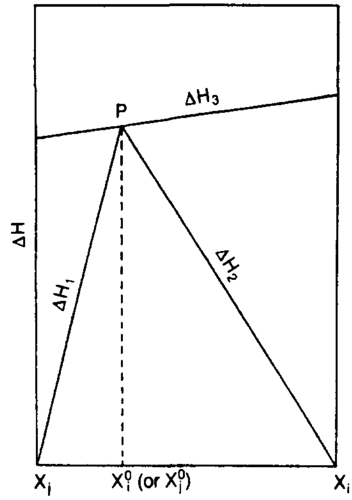

Fig. 1. The dependence of the apparent fusion heat on the composition for a binary system (HX-phase diagram).

Using many values of the eutectic fusion heat obtained by DSC at various mole ratios in the binary system, K_1 in Eq. (2) and K_2 in Eq. (3) can be found by a least-squares regression and, letting $\Delta H_1 = \Delta H_2$ and $X_i = X_i^0$ or $X_j = X_j^0$, the eutectic compositions X_i^0 and X_j^0 can be calculated to be

$$X_i^0 = K_2/(K_1 + K_2) \tag{5}$$

or

$$X_j^0 = K_1/(K_1 + K_2) \tag{6}$$

If the eutectic peak on the DSC curve cannot be separated from the endothermic peak of liquefaction of the remainder of a component in the system, the eutectic compositions can be calculated by means of Eqs. (4) and (2) or (3).

3. Experimental

3.1. Apparatus

The measurements of the apparent fusion heat and eutectic temperature were carried out on a Perkin Elmer DSC-2C instrument at a heating rate of 10 K min^{-1} and with a nitrogen flow rate of $\approx$40.0 cm^3 min^{-1} and a sample size of $\approx$1.5–3.5 mg. The partial area corresponding to the eutectic peak and the total area corresponding to the entire liquefaction of the mixture system on the DSC curve were calculated by using a partial area programme.

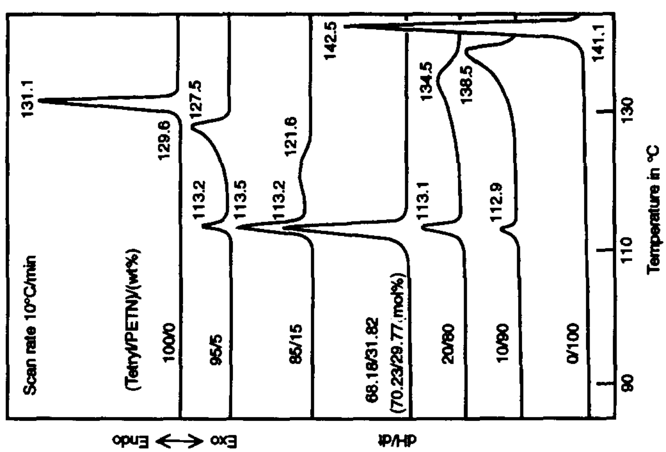

Fig. 2. DSC curves of liquefaction for Tetryl/PETN.

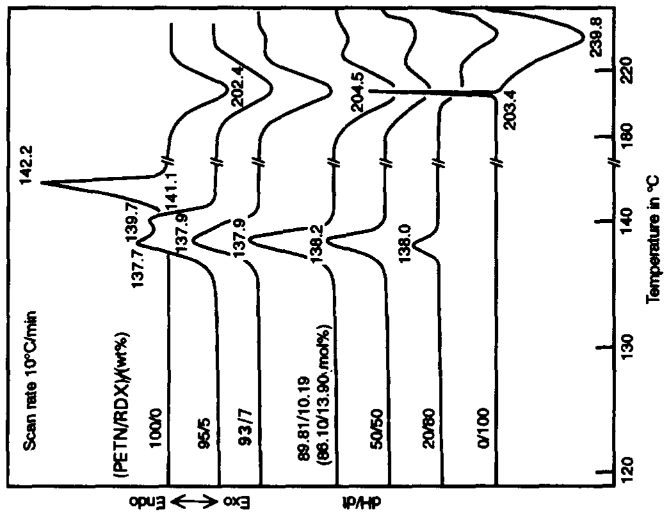

Fig. 3. DSC curves of PETN/RDX.

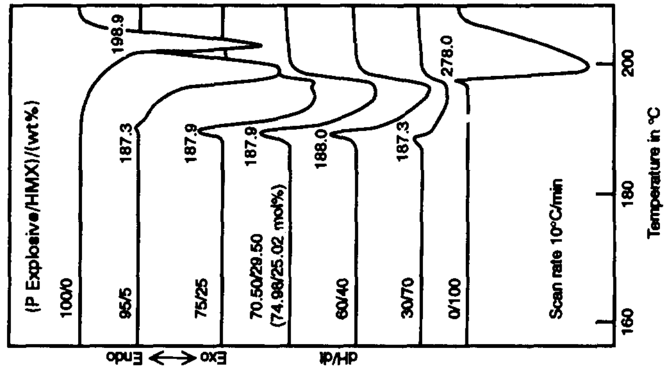

Fig. 4. DSC curves of P Explosive/HMX.

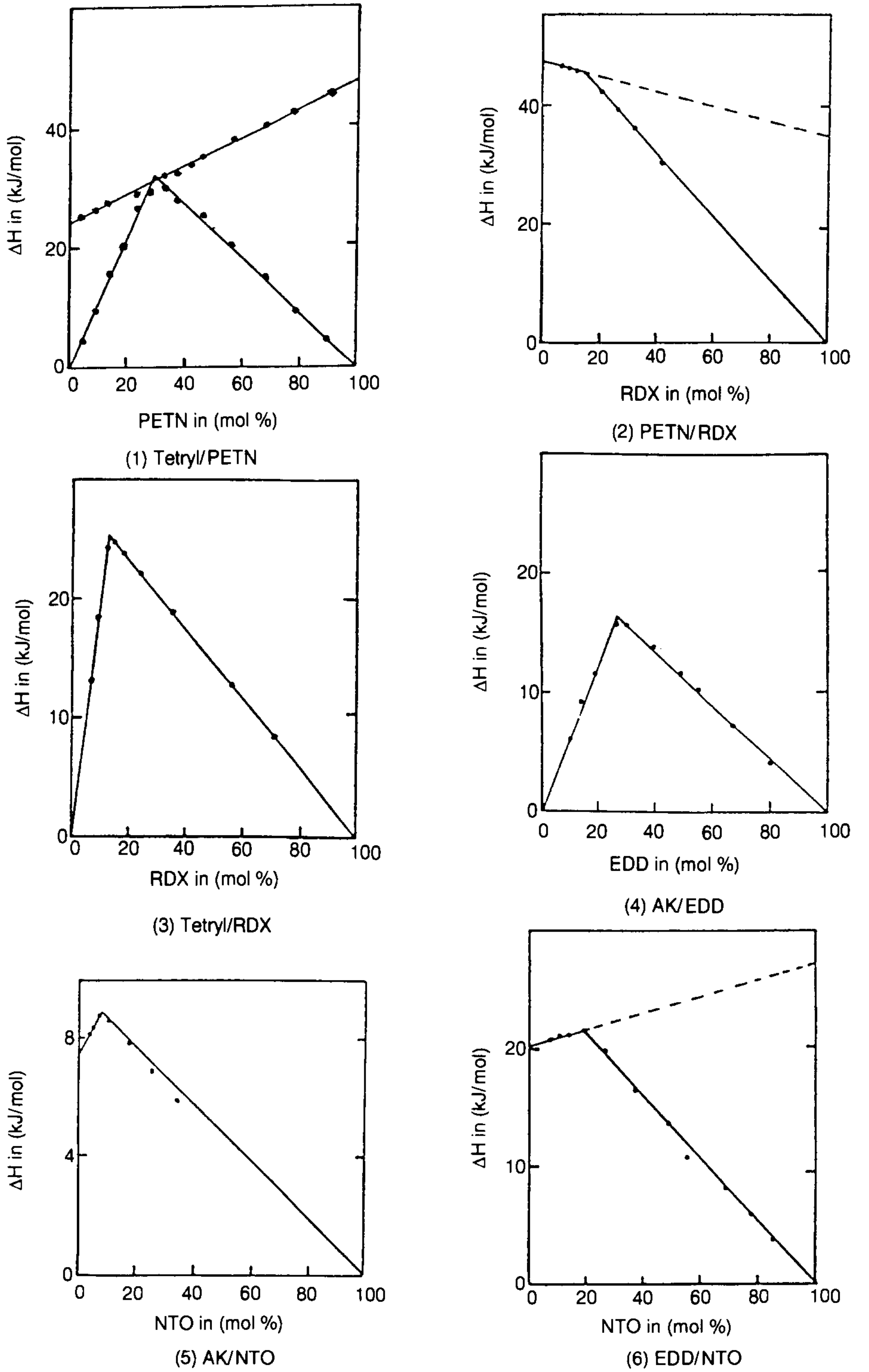
ΔH in (kJ/mol)
PETN in (mol %)
(1) Tetryl/PETN
RDX in (mol %)
(2) PETN/RDX
RDX in (mol %)
(3) Tetryl/RDX
EDD in (mol %)
(4) AK/EDD
NTO in (mol %)
(5) AK/NTO
NTO in (mol %)
(6) EDD/NTO

Fig. 5 (1–6)

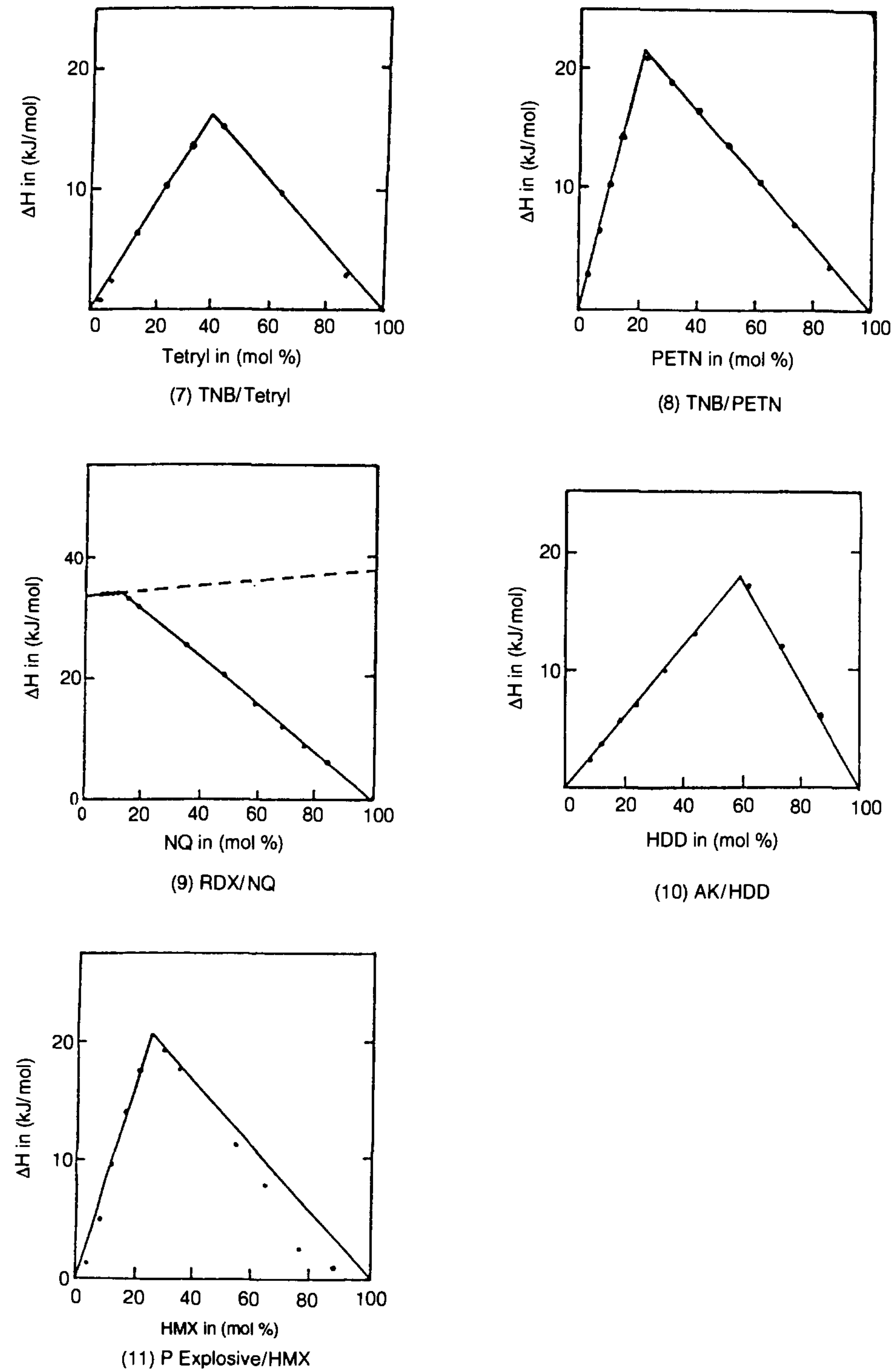

Fig. 5. Dependences of apparent fusion heats on composition (HX-phase diagram) for binary systems of some energetic materials.

Table 1
The eutectic compositions and temperatures of some binary systems

Binary system	Composition/mol%		Temperature/°C	
	HX method	TX method	DSC method	TX method
Tetryl/PETN	70.23/29.77	71.50/28.50	113.2	113.2
PETN/RDX	86.10/13.90	86.37/13.63	137.9	138.0
Tetryl/RDX	87.25/12.75	87.08/12.92	120.9	120.2
AK/EDD	71.95/28.05	72.49/27.51	104.9	104.8
AK/NTO	93.44/6.56	93.37/6.13	145.2	145.4
EDD/NTO	79.83/20.17	79.56/20.44	167.6	167.5
TNB/Tetryl	60.95/39.05	59.81/40.19	84.8	85.2
TNB/PETN	78.19/21.81	78.45/21.55	102.6	102.6
RDX/NQ	86.40/13.60	86.23/13.77	198.5	198.5
AK/HDD	40.24/59.76	39.70/60.30	85.5	85.8
P Explos./HMX	74.98/25.02	–	187.9	–

Table 2
The fusion heats of pure components from HX-phase diagrams and from DSC

Component	Binary system	Fusion heat/(kJ mol^{-1})	
		HX method	DSC method
Tetryl	Tetryl/PETN	24.1	24.4
PETN	Tetryl/PETN	47.6	47.5
PETN	PETN/RDX	47.6	
RDX	PETN/RDX	34.4	33.4
RDX	NQ/RDX	33.5	
AK	NTO/AK	7.5	7.5
EDD	EDD/NTO	20.6	20.8
NTO	EDD/NTO	27.0	–
NTO	NTO/AK	27.0	–
NQ	NQ/RDX	37.5	–

In order to confirm the results obtained by DSC, a hot stage microscope model Boetius, was used to construct the temperature–composition (TX) phase diagrams for binary systems.

3.2. Materials

Ammonium nitrate with 15 wt% potassium nitrate (AK), nitroguanidine (NQ), ethylenediamine dinitrate (EDD), 1,6-hexamethylenediamine dinitrate (HDD), 3-nitro-1,2,4-triazol-5-one (NTO), cyclotrimethylenetrinitramine (RDX), cyclotetramethylenetetranitramine (HMX), 2,4,6-trinitrophenylmethylnitramine (Tetryl),

Table 3
The apparent fusion heat ΔH_{ij} obtained from the TX-phase diagrams of binary systems and the melting points T_i° of the pure components

Binary system X_1/X_2	$T_1^\circ/^\circ C$	$T_2^\circ/^\circ C$	$\Delta H_{12}/(J\ mol^{-1})$	$\Delta H_{21}/(J\ mol^{-1})$
Tetryl/PETN	129.6	141.1	26140.7	59277.2
PETN/RDX	141.1	204.1	59097.5	50862.1
Tetryl/RDX	129.6	204.1	20543.2	38462.9
AK/EDD	159.6	188.6 (EDD_I)	7933.2	20516.0
		173.2 (EDD_{II})		26419.0
AK/NTO	159.6	266.2	9944.1	44336.0
EDD/NTO	188.6	266.2	19795.0	31699.5
TNB/Tetryl	121.2	129.6	17610.6	25022.7
TNB/PETN	121.2	141.1	16977.5	46760.4

2,4,6-trinitrobenzene (TNB), pentaerythritol tetranitrate (PETN), and P Explosive, a nitramine compound.

4. Results and discussion

4.1. The HX-phase diagrams of binary systems

Some typical DSC curves of liquefaction for binary systems of Tetryl/PETN, PETN/RDX and P Explosive/HMX are shown in Figs. 2–4. The HX-phase diagrams of the binary systems of some energetic materials are shown in Fig. 5.

The eutectic compositions of these binary systems from the HX method and their eutectic temperatures measured by DSC are shown in Table 1.

If the eutectic peak on the DSC curves cannot be separated from the endothermic peak of liquefaction of the remainder of a component, e.g. PETN in PETN/RDX, RDX in NQ/RDX, AK in AK/NTO and EDD in EDD/NTO, the eutectic compositions can be calculated by using Eqs. (2) and (4).

On the basis of the facts that the line ΔH_3 in Eq. (4) representing the composition dependence of the total apparent fusion heat for the Tetryl/PETN system and the lines ΔH_1 and ΔH_2 in Eqs. (2) and (3) representing those of the eutectic intersect at a point (see Fig. 1), and that the fusion heats obtained from the extrapolation of Eq. (4) for each component of the systems in Table 2 are in better agreement with the results from another system, or with those determined by DSC for the pure components, it is evident that the above assumptions for Eq. (1) are acceptable to a certain extent for these energetic materials.

There are three types among these binary systems. The first type is a system in which both components decompose on melting, e.g. P Explosive/HMX; the second type is one in which only one component decomposes on melting, e.g. NTO in

EDD/NTO and AK/NTO and NQ in NQ/RDX, and the third contains no component that decomposes, as exemplefied by the removing systems in this paper.

It is worthwhile pointing out that the fusion heat of materials for which decomposition occurs at melting can be found from HX-phase diagram of a binary system in which it is mixed with a component for which no decomposition occurs on melting. For example, the fusion heat of pure NTO was determined from both NTO/EDD and NTO/AK systems to be 27.0 kJ mol^{-1}, and that of NQ from NQ/RDX was found to be 37.8 kJ mol^{-1}. This fusion heat has not been determined by existing methods.

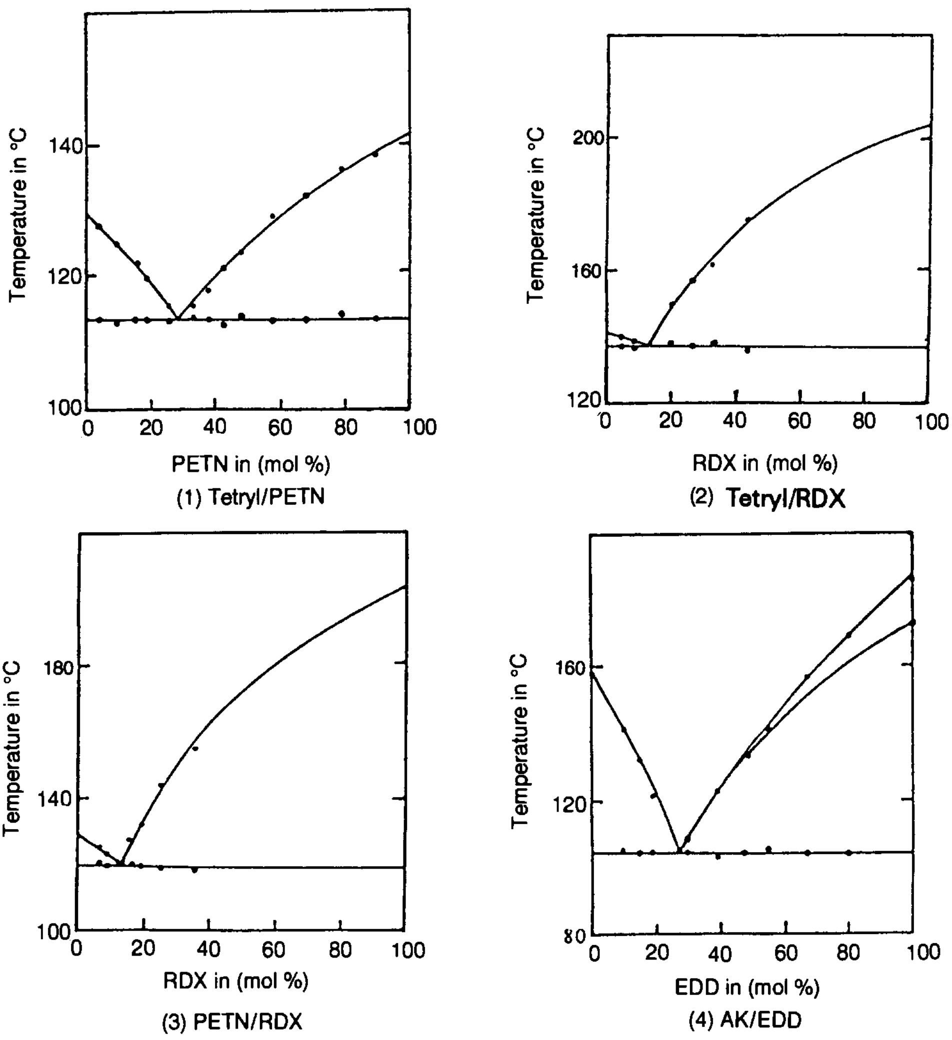

Fig. 6 (1–4)

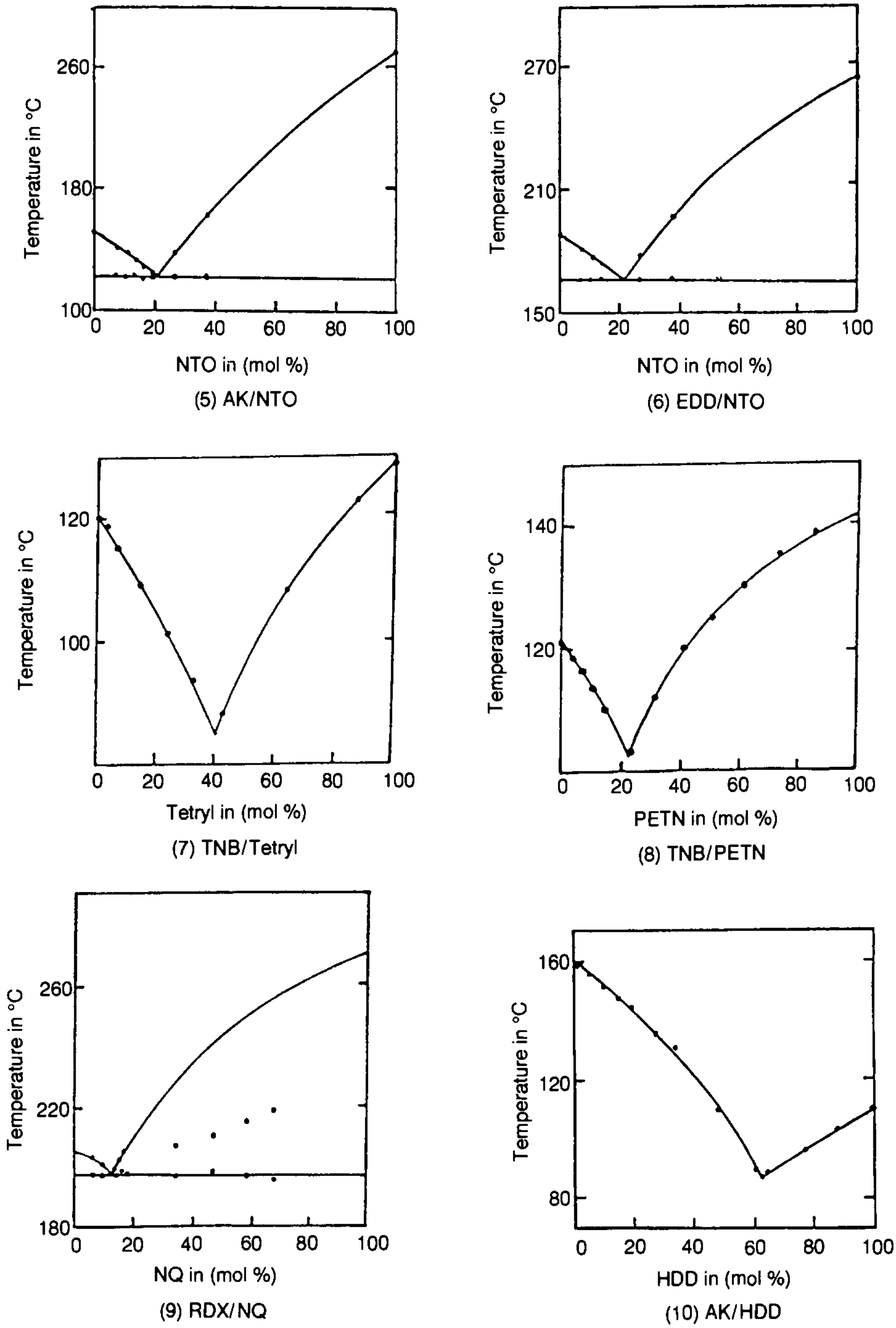

Fig. 6. Dependences of the liquidus temperatures on composition (TX-phase diagram) for binary systems of some energetic materials.

4.2. The TX-phase diagrams of binary systems

In order to confirm the results obtained by the HX method, the TX-phase diagrams of these binary systems were constructed by using the equation

$$\ln X_i = \frac{\Delta H_{ij}}{R}\left(\frac{1}{T_i^0} - \frac{1}{T_i}\right) \quad (7)$$

where X_i is the mole fraction of component i, T_i^0 and T_i are the melting points of pure component i and its liquidus temperature in the binary system respectively, ΔH_{ij} is the apparent fusion heat of component i in the presence of another component j, and R is the gas constant.

The values of T_i were measured with a hot stage microscope. The TX-phase diagrams of these binary systems, except for the system of P Explosive/HMX, are shown in Fig. 6.

The eutectic compositions and temperatures of these systems and the ΔH_{ij} values obtained by Eq. (7) are shown in Tables 1 and 3, respectively.

The results shown in Table 1 show that the eutectic composition and temperatures of these systems obtained from the HX method using DSC are in good agreement with those of the TX method. However, the application of the TX method in determining the liquidus temperatures of mixed systems meets with difficulties when constructing the TX-phase diagram of energetic materials which are characterized by almost simultaneous fusion and decomposition. As a typical example, the TX-phase diagram of P Explosive/HMX cannot be constructed owing to their thermal decomposition at the liquidus temperature. Additionally, when the mole fraction of component NQ in the RDX/NQ system is significantly above that of the eutectic composition, the liquidus temperature of the remaining NQ deviates from the liquidus line by reason of the liquefaction, making NQ decompose more quickly; the greater the mole fraction of NQ, the more marked the decrease in its liquidus temperature (see Fig. 6 (No. 7)). This phenomenon is also exhibited by the HX-phase diagram of P Explosive/HMX (see Fig. 5 (No. 11)).

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