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Measurement of the eutectic composition and temperature of energetic materials. Part 2. The HX-phase diagram of ternary systems

Cui-Mei Yin, Zi-Ru Liu *, Ying-Hui Shao, 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 four ternary systems of energetic materials (including Tetryl/PETN/RDX, AK/EDD/NQ, AK/EDD/NTO and AK/HDD/NTO) were obtained by constructing a special phase diagram for correlation of the apparent fusion heat with the composition (HX-phase diagram). The results obtained from the HX-phase diagrams were confirmed by the determination of the "melting out eutectic" of these systems using HPLC or UV spectrophotometry.

Keywords: DSC; Energetic material; Eutectic; Ternary system

1. Introduction

In previous work [1] a special phase diagram for the correlation of apparent fusion heat with composition (the HX-phase diagram) for binary systems of energetic materials was constructed by DSC. On the basis of some assumptions, the results in terms of compositions were obtained for simple binary systems in which no solid solution was present but liquids of both components are completely mutually soluble.

The phase diagram of the ternary system becomes complicated and the determination of the composition of its eutectic is very time-consuming. If the assumptions

* Corresponding author.

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for binary systems can also be satisfied for a ternary system of energetic materials, the eutectic composition of this ternary system can be simply determined by mean of the HX-phase diagram. In this work, the HX-phase diagrams of some ternary systems are constructed and their eutectic temperatures are determined by DSC.

2. Principle of the method

If the mole fraction of a component i is a constant M_i, the HX-phase diagram of the ternary system can be obtained on the basis of Eq. (1) of Part 1, (Thermochim. Acta, 250 (1995) 65–76, as shown in Fig. 1.

For $X_i = M_1$ (a constant) $< X_i^0$, we have

$$\Delta H_1 = K_1 X_j \quad (1)$$

for $X_j \leq M_1 X_j^0 / X_i^0$

$$\Delta H_2 = K_2 M_1 \quad (2)$$

for $M_1 X_j^0 / X_i^0 \leq X_j \leq 1 - (X_k^0 / X_i^0 + 1) M_1$

and

$$\Delta H_3 = K_3 (1 - M_1 - X_j) \quad (3)$$

at $X_j \geq 1 - (X_k^0 / X_i + 1) M_1$, where

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

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

$$K_3 = \Delta H_i X_i^0 / X_k^0 + \Delta H_j X_j^0 / X_k^0 + \Delta H_k$$

The subscripts i, j, and k refer to the components and the superscript 0 to the eutectic composition.

In a way similar to that for binary systems, K_1, K_2, and K_3 can be obtained from the apparent fusion heat of the eutectics.

When $\Delta H_1 = \Delta H_2 = \Delta H_3$, we have

$$X_i^0 = M_1 / (1 + X_j' - X_j'') \quad (4)$$

$$X_j^0 = X_j' / (1 + X_j' - X_j'') \quad (5)$$

$$X_k^0 = (1 - M_1 - X_j'') / (1 + X_j' - X_j'') \quad (6)$$

where

$$X_j' = M_1 K_2 / K_1 = M_1 X_j^0 / X_i^0$$

and

$$X_j'' = 1 - M_1 (1 + K_2 / K_3) = 1 - M_1 (1 + X_k^0 / X_i^0)$$

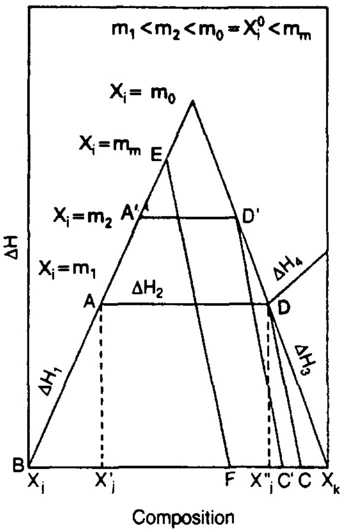

Fig. 1. Dependence of the apparent fusion heat on composition for a ternary system (HX-phase diagram).

In fact, X_j' and X_j'' are the values of the X axis for the intersecting points, A and D in Fig. 1, of a line represented by Eq. (1) with that from Eq. (2), and of a line represented by Eq. (2) with that from Eq. (3), respectively. Now, the HX-phase diagram of the ternary system changes into a trapezium ADCB which is formed by these three lines and the X axis. When X_i is equal to another constant M_2, which is less than X_i^0, the ternary phase diagram consists of another trapezium A′D′C′B. However, when $M_i \geq X_i^0$, the HX-phase diagrams change into a series of triangles, e.g. the triangle EFB. Under the latter condition, the eutectic composition cannot be calculated from this triangle phase diagram. Therefore, in order to calculate the eutectic composition from this HX-phase diagram, an M_i value must be appropriately chosen.

Using many of the values of the eutectic apparent fusion heat obtained by DSC at various mole ratios of two components of the ternary system, where the mole fraction of another component is a suitable constant, K_1, K_2 and K_3 can be found by a least-squares regression from Eqs. (1), (2) and (3), respectively, and the eutectic compositions X_i^0, X_j^0 and X_k^0 can thus be calculated from Eqs. (4), (5) and (6), respectively.

If the ternary eutectic peak on the DSC curve cannot be separated from the binary one formed from the remainder of the other two components, e.g. i and j, the eutectic apparent fusion heat ΔH_3 (Eq. (3)) is substituted by ΔH_4 (Eq. (7)), which is equal to the apparent fusion heat of the ternary eutectic in addition to that of the binary.

$$\Delta H_4 = \Delta H_4^0 + K_4 X_k \tag{7}$$

and

$$X_j'' = 1 - (1 + K_2/K_4)M_i + \Delta H_4^0/K_4$$

where

$$\Delta H_4^0 = \Delta H_i M_1 + \Delta H_j M_1 X_j'/X_i'$$

$$K_4 = \Delta H_k + \Delta H_j X_j^0/X_k^0 - \Delta H_j X_i^0 X_j^1/X_k^0 X_i^1$$

and X_i^1 and X_j^1 are the eutectic compositions in the i, j binary system.

When $X_k = M_1 X_k^0/X_i^0$, Eq. (7) changes to

$$\Delta H_4 = (\Delta H_i + \Delta H_j X_j^0/X_i^0 + \Delta H_k X_k^0 X_i^0) M_1$$

$$= K_2 M_1 = \Delta H_2$$

indicating that the lines of ΔH_4 and ΔH_2 intersect at $X_k = M_1 X_k^0/X_i^0$ or $X_j = 1 - M_1 - M_1 X_k^0/X_i^0$.

When $X_k = 0$, Eq. (7) becomes

$$\Delta H_4 = \Delta H_i M_1 + \Delta H_j M_1 X_j^1/X_i^1$$

i.e., Eq. (2) in Part 1 of this work for a binary system of components i and j.

3. Experimental

3.1. Apparatus

The apparatus for the measurements of the apparent fusion heat and eutectic temperature as well as the measuring conditions are the same as that of Part 1 in this work.

In order to prove the results obtained by DSC, an apparatus described by Szulc et al. [2] was used to obtain the "melting out eutectic", which was quantitatively analysed by high performance liquid chromatography (HPLC) or UV spectrophotometer in order to find the eutectic compositions in ternary systems. The melting out was carried out in a glass funnel with a G4 fritted glass bottom connected to a vacuum flask, which were put into an air thermostat with temperature control. When the ternary mixture of a composition not very distant from the eutectic one was put in the funnel and the temperature of the thermostat was raised to the eutectic temperature, melting out dropped into the flask.

3.2. Materials

2,4,6-Trinitrophenylmethylnitramine (Tetryl), pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), ammonium nitrate with 15 wt% potassium nitrate (AK), nitroguanidine (NQ), ethylenediamine dinitrate (EDD), 1,6-hexamethylenediamine dinitrate (HDD) and 3-nitro-1,2,4-triazol-5-one (NTO).

4. Results and discussion

Some typical DSC curves of liquefaction for the Tetryl/PETN/RDX ternary system are shown in Fig. 2.

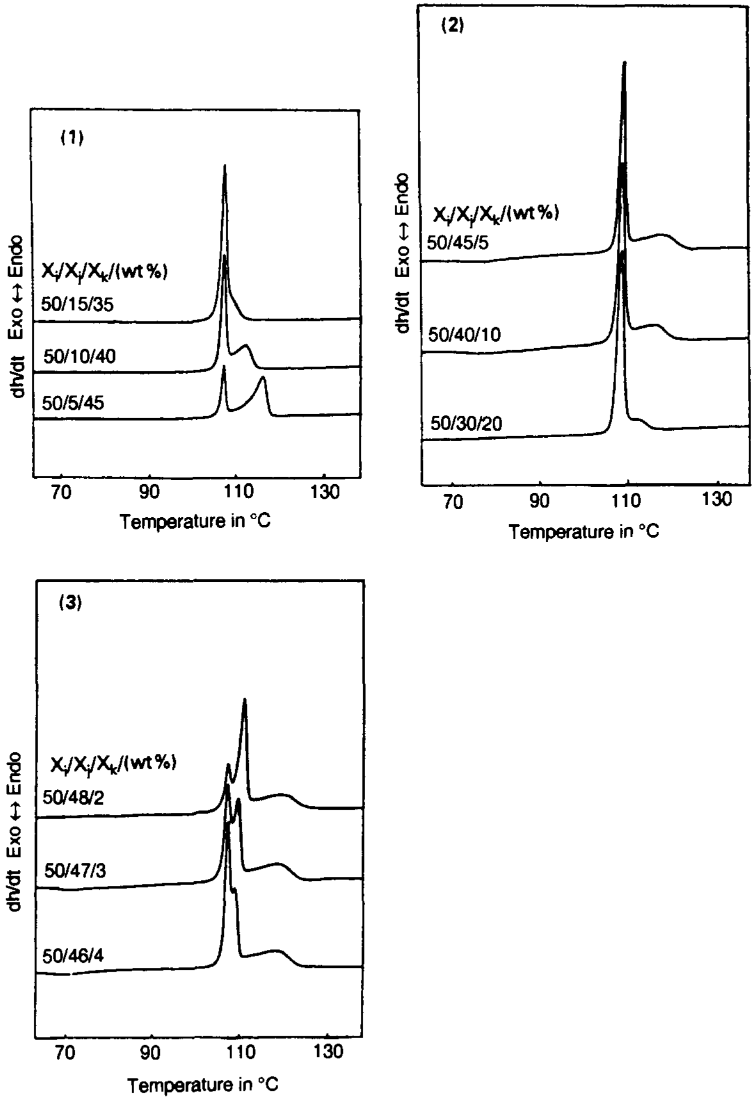

Fig. 2. The DSC curves of $X_i/X_j/X_k$ = Tetryl/PETN/RDX for a fraction ($X_i = M_1$) of Tetryl-50 wt%. (1) $X_j \le M_1 X_j^0/X_i^0$, (2) $M_1 X_j^0/X_i^0 \le X_j \le 1-(X_k^0/X_i^0+1)M_1$, (3) $X_j \ge 1-(X_k^0/X_i+1)M_1$.

The HX-phase diagrams obtained by DSC for the ternary systems of Tetryl/PETN/RDX, AK/EDD/NQ, AK/EDD/NTO and AK/HDD/NTO are shown in Fig. 3. The eutectic compositions calculated from Eqs. (4), (5) and (6) for these four systems and determined by HPLC or UV spectrophotometry for the melting out eutectic of the last three systems and the eutectic temperatures determined by DSC are shown in Table 1.

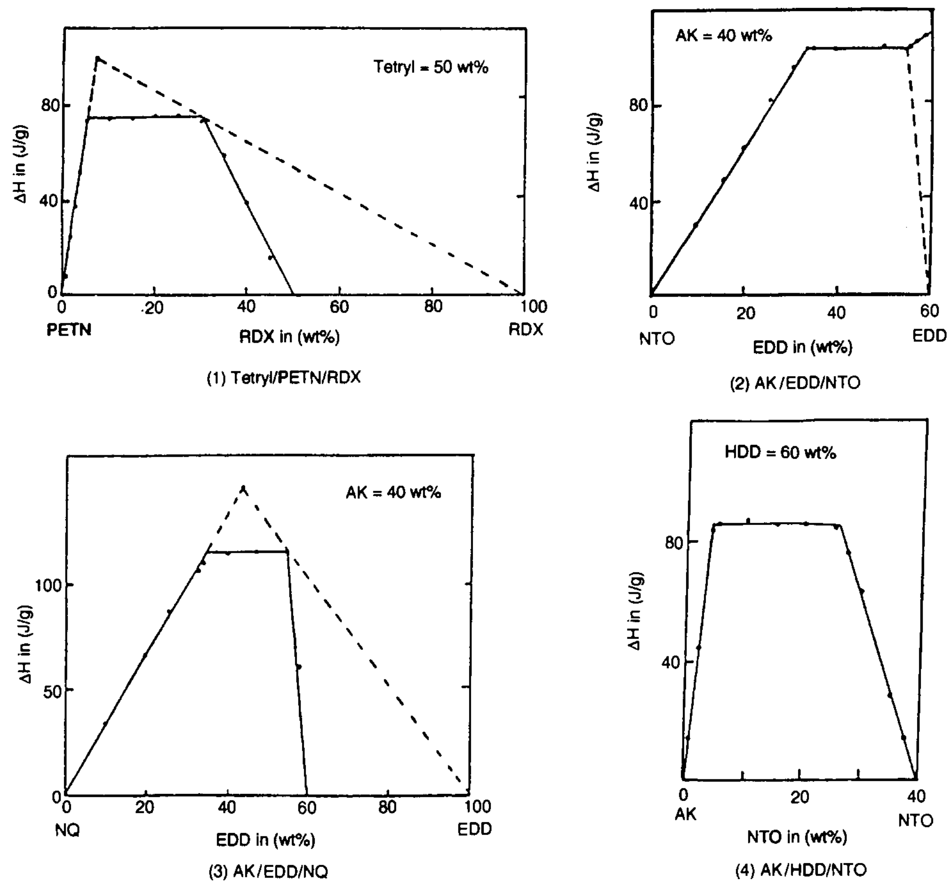

Fig. 3. Dependences of the apparent fusion heats on composition (TX-phase diagram) for ternary systems of some energetic materials. (1) Tetryl/PETN/RDX (2) AK/EDD/NTO (3) AK/EDD/NQ (4) AK/HDD/NTO

Table 1
The eutectic compositions from the HX method and HPLC or UV analyses and the eutectic temperatures by DSC for four ternary systems

System	Eutectic composition/(mol%)		Eutectic temp./°C
	HX method	HPLC or UV analyses	
Tetryl/PETN/RDX	65.99/24.11/9.90	66.96/23.29/9.75	108.3
AK/EDD/NQ [a]	66.94/25.78/7.28	–	98.8
AK/EDD/NTO	69.97/26.09/3.94	NTO = 2.97 [b]	103.5
AK/HDD/NTO	37.55/55.51/6.94	–	64.6

[a] The result for this system was given in the literature [3] as 67.24/25.30/7.44 mol%. [b] Result obtained from UV analysis.

As the ternary eutectic peaks on the DSC curves for the systems AK/EDD/NTO and AK/HDD/NTO cannot be separated from the binary ones formed from the remainder of the AK and EDD components and the AK and HDD components, Eq. (6) was replaced by Eq. (7) for the calculation of the eutectic components.

It is evident from Table 1 that the results of the HX method are in agreement with those obtained from HPLC or UV analyses or literature data within ± 1.0 mol%. In general, the error in measuring or calculating eutectic compositions for binary and ternary systems is within $\pm 2-3$ mol% [4–6], certainly within ± 5 mol% [2]. Obviously the HX method is fairly satisfactory for the measurement of the eutectic composition of binary and ternary systems.

The apparent fusion heats of the eutectics prepared according to the result from the literature for AK/EDD/NQ [3] and according to those of determinations of the above HX-phase diagram for Tetryl/PETN/RDX and the intersecting point of a line represented by Eq. (2) with that from Eq. (3) are respectively located at the top and on the side of the triangles in the corresponding HX-phase diagram. This shows that the principle of the HX method is acceptable for various energetic materials.

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