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An investigation on eutectic binary phase diagram of volatilizable energetic materials by high pressure DSC

Ying-Hui Shao · Xiao-Ning Ren · Zi-Ru Liu

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Abstract The eutectic binary phase diagrams of volatilizable energetic material 1,3,3-trinitroazetidine (TNAZ) with 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1-methyl-2,4-dinitroimidazole (MDNI) have been investigated by high pressure differential scanning calorimeter (PDSC), respectively. The liquefying and melting processes of TNAZ/RDX and TNAZ/MDNI volatilizable systems have been studied. On the basis of the data of apparent fusion heat and liquefying temperature, the phase diagrams of apparent fusion heat (*H*) with composition (*X*) and liquefying temperature (*T*) with composition (*X*) were constructed, respectively. The results showed that the gasification or volatilization of easy volatile energetic materials could be efficiently restrained by high pressure atmosphere, and the perfect and ideal phase diagrams can be constructed. The eutectic temperatures for TNAZ/RDX and TNAZ/MDNI are measured to be 95.5 and 82.3 °C, respectively. The eutectic compositions of mole ratios for the two systems are obtained to be 93.55/6.45 (*T*–*X* method), 93.79/6.21 (*H*–*X* method) and 62.25/37.75 (*T*–*X* method), 63.29/33.71 (*H*–*X* method), respectively.

Keywords Physics chemistry · PDSC · Volatilizable energetic materials · Binary system · Phase diagram

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Introduction

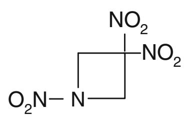
1,3,3-Trinitroazetidine (TNAZ), which was synthesized by American chemist in 1983 year firstly[1–3], is a high energy density material. It has some merit such as high energy, lower sensitivity, high decomposition temperature, and good stability [4]. Especially, it has lower melting point, could form eutectic systems with many usual explosives [5, 6] as a good casting explosive or low vulnerability intermolecular explosive. The binary system of TNAZ/RDX has been already studied at ambient pressure, but a perfect phase diagram cannot be constructed owing to the strong volatilization of molten TNAZ at ambient pressure and higher temperature [7], and the higher melting point and a property of decomposition on melting for RDX [8]. 1-Methyl-2,4-dinitroimidazole (MDNI) is a new energetic material, has some merit such as high energy and low sensitivity [9], also is a potential material used as the casting explosive or low vulnerability intermolecular explosive. It has higher melting point and higher decomposition temperature, but also is a volatile material. Because the volatilization of molten TNAZ is strong at ambient pressure and the liquidus temperature of MDNI, a right and perfect binary system of TNAZ/MDNI cannot also be constructed. Therefore, in order to inhibit the volatilization of molten TNAZ and MDNI, a high pressure differential scanning calorimeter (PDSC) was used to investigate the melting and liquefying processes for these two binary systems at 1 MPa nitrogen atmosphere. In reality, in order to inhibit the volatilization, PDSC were already used to study the compatibilities of TNAZ with some energetic materials [5] and thermal decompositions of some volatile materials [6–8, 10].

The methods used in this works were reported previously [6, 8, 11], in which the *H*–*X* phase diagram is constructed by the correlation of the apparent fusion heat (H) with the composition (X), viz., H–X method, and the T–X phase diagram by the correlation of the liquidus temperature (T) with the composition (X), viz., T–X method.

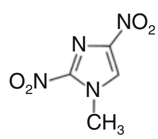
Experimental

Materials

TNAZ (1,3,3-trinitroazetidine) and MDNI (1-methyl-2,4-dinitroimidazole), the structural formula are



and



and RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), these three samples were all prepared by *Xi'an Modern Chemistry Research Institute* and their purity quotients were determined by liquid chromatogram to be higher than 99.9%.

All mixing mass ratios of tested samples for two systems of TNAX with RDX and MDNI are 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90 and 0:100, respectively.

Apparatus and experiment conditions

TA Model DSC 910S differential scanning calorimeter has been applied to measure the apparent fusion heats and the liquidus temperatures of the two systems with various mixing ratios, All DSC tests were carried out in static atmosphere of 0.1 and 1 MPa and at a heating rate of 10 K min^{-1}, using sample size of 8.00 ± 0.1 mg and aluminum crucible. On PDSC tests, the mixture samples were heated till entire liquefying at lower decomposition temperatures, when the samples were cooled to entire solidification and they were heated again to obtain PDSC curves.

TA Model TGA 2950 thermogravimetric analysis with DTG has been applied to observe the thermal behavior of TNAZ and MDNI at ambient pressure. TG-DTG tests were carried out in dynamic atmosphere of nitrogen gas of 100 mL min^{-1} and at a heating rate of 10 K min^{-1}, using sample size of ca. 2 mg and aluminum crucible.

Results and discussion

TNAZ/RDX system

Behavior of melting or liquefying for TNAZ/RDX system on PDSC

Figure 1 shows the DSC and TG-DTG curves of TNAZ (1,3,3-trinitroazetidine), which were from literature [8]), and its PDSC curves are shown in Fig. 2. As seen from Fig. 1, besides an endothermic melting peak on DSC curve of TNAZ, there is a wide temperature range of endothermic process, which corresponds to a mass loss on TG curve. As seen from the TG curve, the residual mass of TNAZ was almost zero at 240 °C. These results indicate that molten TNAZ is an easiest volatilizing or gasifying material. As seen from Fig. 2, at 1 MPa no endothermic process of gasification or volatilization could be observed, whereas

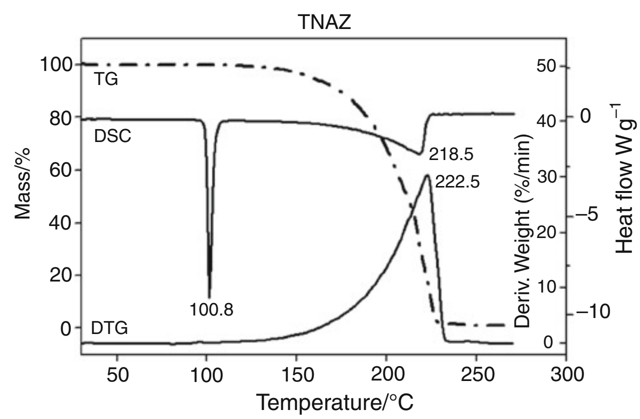


Fig. 1 DSC curve and TG-DTG curve of TNAZ at ambient pressure

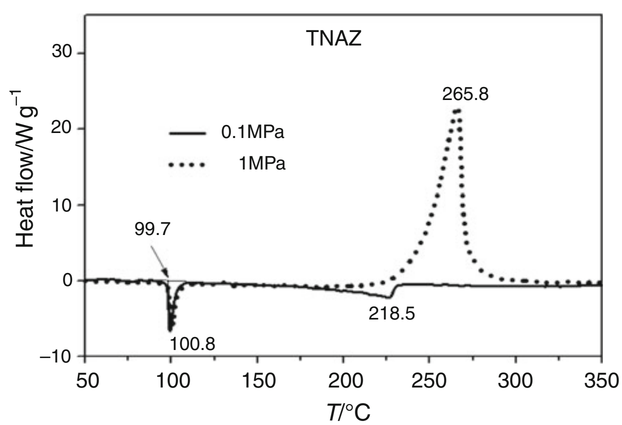


Fig. 2 PDSC curves of TNAZ at 0.1 MPa ambient pressure and 1 MPa static pressure

an exothermic decomposition appears on PDSC curve of TNAZ. The results indicate that the gasification or volatilization of TNAZ can be inhibited efficiently by elevated pressure.

In our previous work, it was found that when we used DSC data of TNAZ/RDX at 0.1 MPa to investigate the melting and liquefying processes of the binary system, perfect T–X and H–X phase diagrams could not be obtained (refer to literature [8]). Although it is related to that RDX decomposes on melting and has higher melting point, a main reason for this is that TNAZ is the easiest volatile or gasified material.

In order to restrain the volatilization or gasification of TNAZ efficiently, the melting and liquefying processes of the TNAZ/RDX system were investigated under 1 MPa surroundings ambience. PDSC curves and its characteristic values for TNAZ/RDX mixture systems at various mass percents are shown in Fig. 3 and Table 1, respectively. In Table 1, the symbols: T_e—eutectic temperature, T_L—liquidus temperature of the system, T_m—melting point of pure material, ΔH_{eu}—eutectic fusion heat, ΔH—total fusion heat of the system, similarly hereinafter.

As seen from Fig. 3 and Table 1, the system of TNAZ/RDX is an eutectic system with the average eutectic temperature of 95.5 °C or 368.7 K. The other endothermic peak on PDSC curve is the liquidus process of the remaining component.

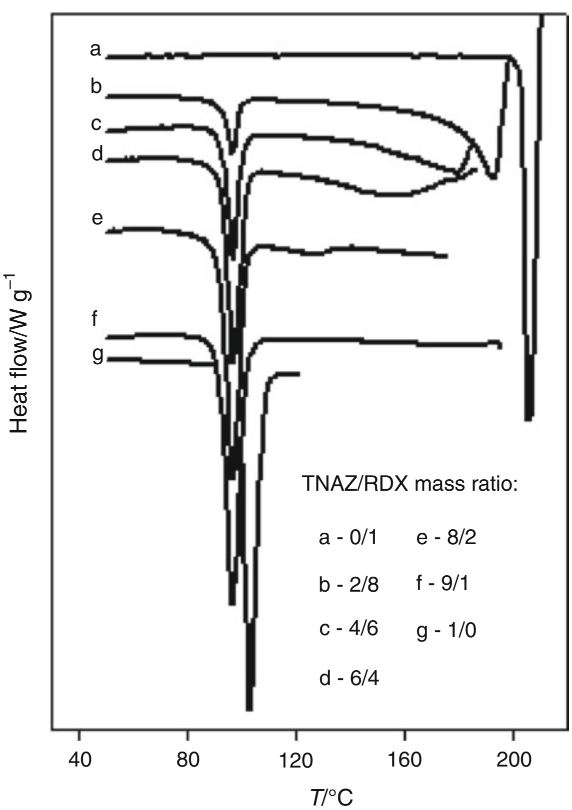


Fig. 3 PDSC curves of TNAZ/RDX system at 1 MPa static pressure

T–X phase diagram of TNAZ/RDX system

The liquidus temperature obtained from DSC or PDSC must be corrected by a way, in which T_L is equal to the end temperature of liquidus peak of mixture system minus the melting temperature range of the eutectic on DSC curve (see literature [6, 8]).

Using the data in Table 1, the T–X phase diagram for correlation of liquidus temperature, T_L, with the mole percentage X_T of TNAZ was constructed, and the result is shown in Fig. 4.

On the basis of liquidus temperature equation for binary system [8, 11]

$$\ln X = \frac{\Delta H}{R}\left(\frac{1}{T^0} - \frac{1}{T}\right) \quad (1)$$

using the T_L values in TNAZ/RDX mass ratio range from 0/100 to 90/10, the correlation equation of X_R, which is the mole fraction of RDX component, with T_L can be obtained by a least-squares regression, as follows:

$$\ln X_R = 9.2205 - 4409.9/T_L \quad \text{(regression correlation coefficient } r = 0.9923) \quad (2)$$

when $T_L = T_e = 368.7$ K, the eutectic compositions of TNAZ/RDX system can be obtained from Eq. 2 to be 93.55/6.45 for mole ratio.

H–X phase diagram of TNAZ/RDX system

According to the principle of the linear relation of eutectic fusion heat ΔH_{eu} with the composition content X [8, 11], the H–X phase diagram was constructed by using the data in Table 1, as shown in Fig. 5.

The correlation equations of eutectic fusion heat ΔH_{eu} and total fusion heat of the system with the mass percentage X_T of TNAZ can be obtained by a least-squares regression, respectively, as follows:

$$\Delta H_1 = 1.4467 X_T \quad (k_1 \text{line in Fig.5}, X_T = 0 - 90 \text{ mass\%}) \quad (r = 0.9977) \quad (3)$$

$$\Delta H_3 = 150.0 - 0.169 X_T \quad (k_3 \text{ line in Fig.5}, X_T = 0 - 100 \text{ mass\%}) \quad (r = 0.9789) \quad (4)$$

when $\Delta H_1 = \Delta H_3$, the eutectic compositions of TNAZ/RDX system can be obtained from Eqs. 3 and 4 to be

Table 1 PDSC characteristics of TNAZ/RDX system at 1 MPa

TNAZ/RDX (mass ratio)	TNAZ/RDX (mole ratio)	ΔH_{eu}/J g^{-1}	ΔH/J g^{-1}	T_e or T_m/°C	T_L/°C
0:100	0:100	0.0	150.8	203.5	203.5
20:80	22.43:77.57	24.5	146.9	93.4	189.5
30:70	33.14:66.86	40.7	145.1	95.2	183.2
40:60	43.54:56.46	56.8	142.5	96.4	181.0
50:50	53.63:46.37	74.3	142.2	95.5	175.0
60:40	63.44:36.56	83.2	140.0	95.7	163.2
70:30	72.97:27.03	101.0	135.7	97.4	153.5
80:20	82.22:17.78	114.7	136.2	95.4	131.7
90:10	91.24:8.76	135.0	135.0	96.3	99.1
92:8	93.01:6.99	127.0	–	96.3	99.3
95:5	95.65:4.35	114.6	–	95.2	95.6
98:2	98.27:1.73	98.0	–	98.3	98.3
100:0	100:0	0.0	135.0	99.7	99.7

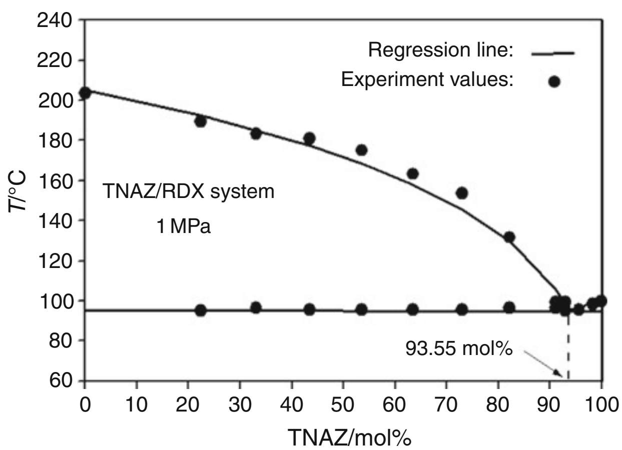


Fig. 4 *T–X* phase diagram of TNAZ/RDX binary system at 1 MPa

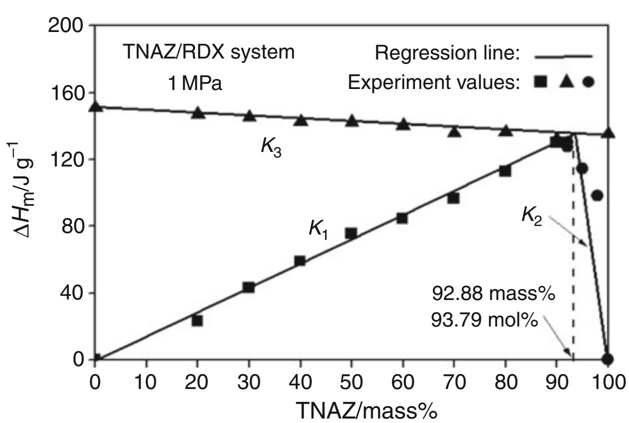


Fig. 5 *H–X* phase diagram of TNAZ/RDX binary system at 1 MPa

92.88/7.12 for mass ratio or 93.79/6.21 for mole ratio. These results are good consistent with those obtained from above *T–X* method.

Comparison between the phase diagrams at ambient and elevated pressure

Figures 6 and 7, which have been drawn from literature[8], are the *T–X* and *H–X* phase diagrams of TNAZ/RDX at ambient pressure (0.1 MPa), respectively. In comparison to Figs. 4 and 5, the two binary phase diagrams at 0.1 MPa are non-perfect. The reason for this is that the system of TNAZ/RDX has a higher eutectic temperature and the higher liquidus temperatures, so that higher TNAZ content in eutectic composition leads to the higher volatility. When TNAZ in the system has high content and the liquefying process appears at higher temperature, the molten TNAZ in mixture system could be largely volatilized or gasified. In this case, the measured value of liquidus temperature could be higher than that of calculation from Eq. 1, thus the perfect *T–X* phase diagram cannot be constructed. Besides,

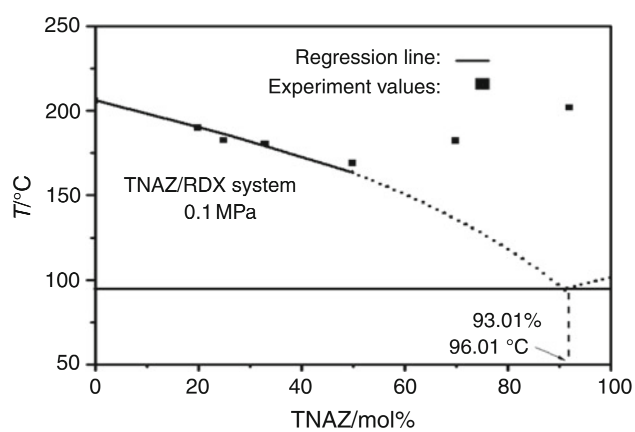


Fig. 6 *T–X* phase diagram of TNAZ/RDX binary system at 0.1 MPa pressure (from literature [8])

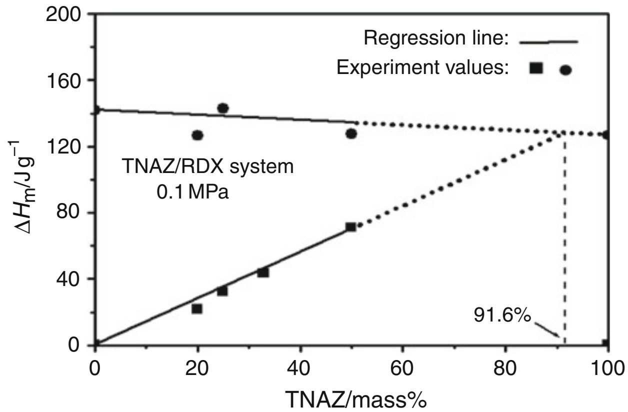


Fig. 7 *H–X* phase diagram of TNAZ/RDX binary system at 0.1 MPa pressure (from literature [8])

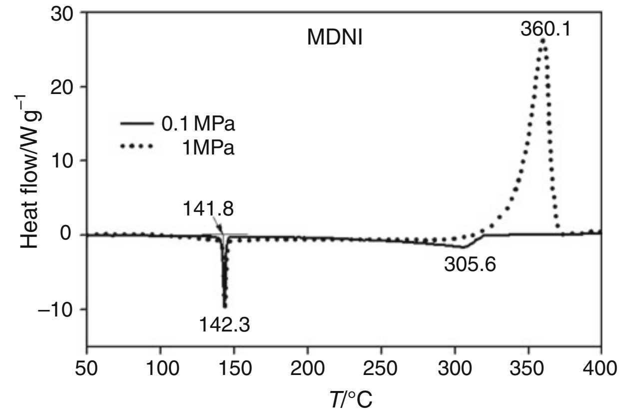


Fig. 9 PDSC curves of MDNI at 0.1 MPa and 1 MPa static pressure

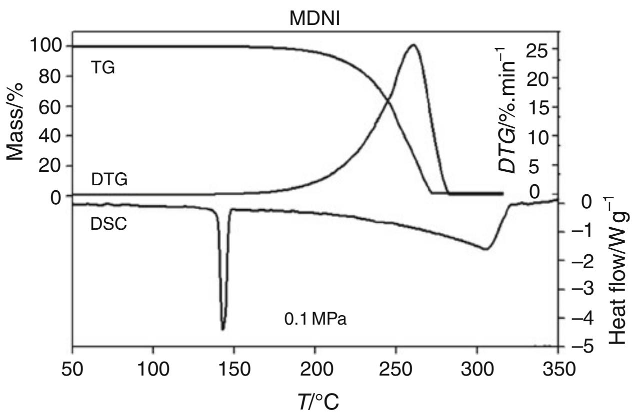


Fig. 8 DSC and TG-DTG curves of MDNI at 0.1 MPa static pressure

when TNAZ has high content, the remaining TNAZ during liquefying process and the TNAZ composition in the eutectic during melting process could be largely volatilized or gasified, thus the perfect *H–X* phase diagram also cannot be constructed.

There is the difference between the eutectic compositions obtained from Figs. 6 and 7 and from above results at 1 MPa, because the data obtained from Figs. 6 and 7 are the extrapolated values at 0.1 MPa. Therefore, the data obtained from 1 MPa must be considered as the more reliable.

TNAZ/MDNI system

Behavior of melting or liquefying for TNAZ/MDNI system on DSC and PDSC

MDNI (1-methyl-2,4-dinitroimidazole) is a new energy material, which has some merits such as high energy and low sensitivity [9]. It has higher melting point and higher decomposition temperature.

The curves of DSC, TG-DTG, and PDSC for MDNI at ambient pressure (0.1 MPa) are shown in Figs. 8 and 9, respectively. It is found from Figs. 8 and 9 that the MDNI, similar to TNAZ, also is a volatile material and the volatilization or gasification of MDNI can be efficiently restrained at elevated pressure of 1 MPa.

Therefore, the mixed system formed from MDNI and TNAZ will be the easiest volatile or gasified. Although the melting point of MDNI is higher, its value is lower than that of RDX. And, when the melting and liquefying process of TNAZ/MDNI system have been examined, the testing temperatures do not exceed too higher than the melting point of MDNI, here the volatilization or gasification of MDNI would be insignificant. Thus, the influence on the measurements of melting heat and liquidus temperature for TNAZ/MDNI system is attributed to the easiest volatilization or gasification of TNAZ.

PDSC curves of TNAZ/MDNI system at 1 MPa are shown in Fig. 10. The characteristic values of melting and liquefying on DSC (0.1 MPa) and PDSC (1 MPa) for TNAZ/MDNI system are listed in Table 2.

It is found from Fig. 10 and Table 2 that the system of TNAZ/MDNI is an eutectic system with the eutectic temperature average of 82.3 °C (or 355.5 K) for 1 MPa and 82.1 °C for 0.1 MPa.

T–X phase diagram of TNAZ/MDNI system

Using the data in Table 2, the *T–X* phase diagram for correlation of liquidus temperature T_L with the mole percentage X_T of TNAZ was constructed, as shown in Fig. 11. Using the T_L values in TNAZ/MDNI, mass ratio ranged from 0/100 to 60/40 at 1 MPa pressure, on the basis of liquidus temperature equation (Eq. 1), the correlation equation of X_M, which is the mole fraction of MDNI

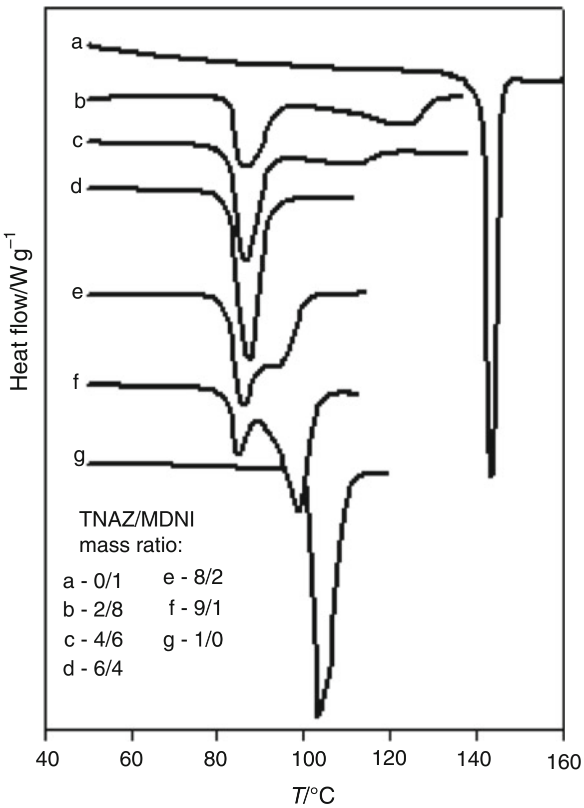


Fig. 10 PDSC curves of TNAZ/MDNI system at 1 MPa static pressure

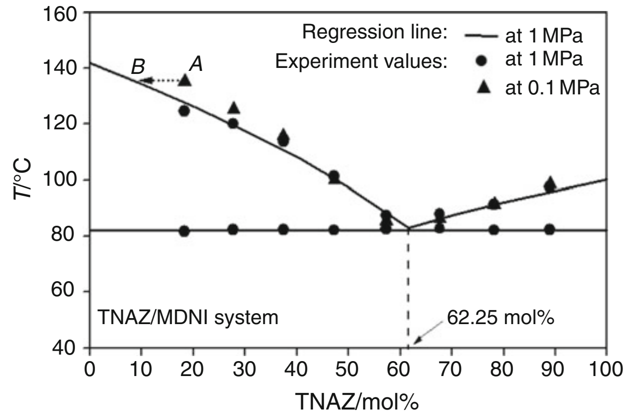


Fig. 11 *T–X* phase diagram of TNAZ/MDNI binary system

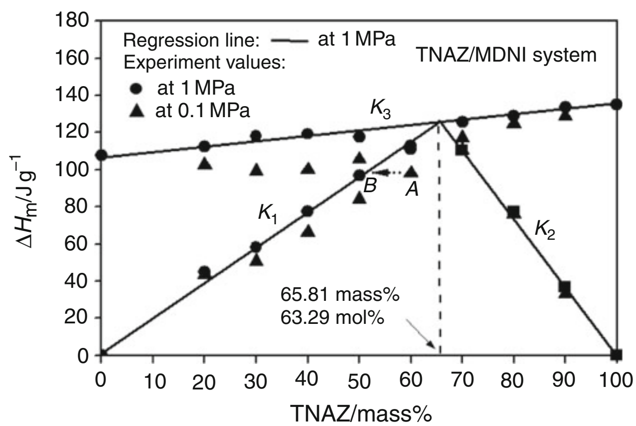


Fig. 12 *H–X* phase diagram of TNAZ/MDNI binary system

component, with T_L can be obtained by a least-squares regression, as follows

$$\ln X_M = 5.8227 - 2416.3/T_L \quad (r = 0.9979) \tag{5}$$

when $T_L = T_e = 355.5$ K, the eutectic compositions of TNAZ/MDNI system can be obtained from Eq. 5 to be 62.25/37.75 for mole ratio.

H–X phase diagram of TNAZ/MDNI system

Using the data of the eutectic fusion heat ΔH_{eu} and total fusion heat of the system at 1 MPa in Table 2, the *H–X* phase diagram of TNAZ/MDNI system was constructed as shown in Fig. 12.

Table 2 PDSC characteristics of TNAZ/MDNI system at 0.1 and 1 MPa

TNAZ/MDNI (mass ratio)	TNAZ/MDNI (mole ratio)	ΔH_{eu}/J g^{-1}		ΔH/J g^{-1}		T_e or T_m/°C		T_L/°C	
		1 MPa	0.1 MPa	1 MPa	0.1 MPa	1 MPa	0.1 MPa	1 MPa	0.1 MPa
0:100	0:100	0.0	0.0	107.9	107.9	141.9	141.7	141.8	141.7
20:80	18.30:81.70	45.1	43.5	112.6	102.5	81.7	81.6	124.9	135.1
30:70	27.74:72.26	58.1	50.6	118.0	99.1	82.3	81.5	120.1	125.1
40:60	37.39:62.61	77.5	66.0	119.3	99.8	82.2	81.9	113.6	115.7
50:50	47.25:52.75	96.9	84.2	117.7	105.5	82.1	82.2	101.3	99.9
60:40	57.33:42.67	111.1	98.0	113.2	112.4	82.7	82.5	87.8	85.4
70:30	67.64:32.36	110.5	110.5	125.8	117.0	82.8	82.2	87.9	86.3
80:20	78.18:21.82	75.7	75.7	129.1	124.7	82.2	82.2	92.6	91.3
90:10	88.97:11.03	33.0	33.0	133.6	128.6	82.3	82.4	97.5	98.5
100:0	100:0	0.0	0.00	135.0	127.0	99.7	99.7	99.7	99.7

The correlation equations of eutectic fusion heat ΔH_{eu} with TNAZ content X_T ranges from 0 to 60 mass% and from 70 to 100 mass% can be obtained by a least-squares regression, respectively, as follows:

$$\Delta H_1 = 1.9173X_T \quad (k_1\text{line in Fig.12, } X_T = 0 - 60 \text{ mass\%}) \quad (r = 0.9960) \tag{6}$$

$$\Delta H_2 = 369.65 - 3.70X_T \quad (k_2\text{line in Fig.12, } X_T = 70 - 100 \text{ mass\%}) \quad (r = 0.9993) \tag{7}$$

when $\Delta H_1 = \Delta H_2$, the eutectic compositions of TNAZ/MDNI system can be obtained from Eqs. 6 and 7 to be 65.81/34.19 for mass ratio or 63.29/33.71 for mole ratio. These results are consistent with those obtained from above *T–X* method.

Comparison between the DSC characteristics at ambient and elevated pressure

There is an evident influence of volatilization or gasification of two components in TNAZ/MDNI, especially TNAZ, on the two methods constructed phase diagram from measurements of melting heat and liquidus temperature. In order to prove the influence, DSC measurements of various ratios of TNAZ/MDNI were carried out at 0.1 MPa. The characteristic values obtained from the DSC tests are also listed in Table 2 and shown in Figs. 11 and 12.

It is found from Figs. 11 and 12 that when the content of TNAZ is lower than its eutectic composition, the liquidus temperature T_L of MDNI at 0.1 MPa is higher than that at 1 MPa in same mixing ratio. And, the higher the liquidus temperature of MDNI is, the greater the deflection is. The eutectic fusion heat ΔH_{eu} at 0.1 MPa is lower than that at 1 MPa in same mixing ratio. Also, the more adjacent to the eutectic composition is, the greater the deflection is.

The reason for these deflections is that MDNI has a higher melting point. When the content of MDNI is higher (or that of TNAZ is lower), the liquidus temperature T_L of MDNI is many higher than the melting point of TNAZ. In this case, the volatilization or gasification of molten TNAZ would be promoted, resulting in the decrease of relative content of TNAZ or the increase of relative content of MDNI in system. As a consequence, so as the T_L measured by DSC test to correspond to that obtained from lower content of TNAZ mixed system, as such the "A" point corresponds to the "B" point in Fig. 11. Similarly, the eutectic fusion heat ΔH_{eu} would be decreased by the volatilization or gasification of molten TNAZ and its measured values at 0.1 MPa corresponds merely to that obtained from lower content of TNAZ mixed system, as such the "A" point returns to the "B" point in Fig. 12. The sum ΔH of the fusion heat and the liquidus heat can be also affected by the volatilization or gasification of molten TNAZ.

Therefore, the *T–X* and *H–X* phase diagrams for the easiest volatile systems could be not constructed and true eutectic compositions could be not obtained from the data at ambient pressure.

Conclusions

The volatilization or gasification of molten component in mixed system could be efficiently restrained by high pressure atmosphere, which provides way to construct the binary phase diagram of the systems with the easiest volatile and the higher melting point components or with two easiest volatile components. The perfect and ideal phase diagrams of the *T–X* and *H–X* for TNAZ/RDX and TNAZ/MDNI binary systems can be constructed by PDSC.

The eutectic temperatures for TNAZ/RDX and TNAZ/MDNI are measured to be 95.5 and 82.3 °C, respectively. The eutectic compositions of mole ratios for the two systems are obtained to be 93.55/6.45 (*T–X* method), 93.79/6.21 (*H–X* method) and 62.25/37.75 (*T–X* method), 63.29/33.71 (*H–X* method), respectively.

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