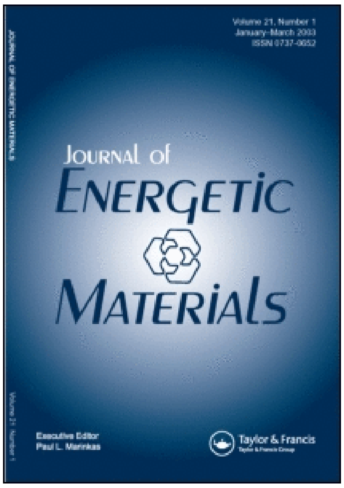


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# Binary phase diagram series: 1,3,3-trinitroazetidine (TNAZ)/*n*-nitroso-3,3-dinitroazetidine (ONDNAZ)

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## BINARY PHASE DIAGRAM SERIES:

## 1,3,3-TRINITROAZETIDINE (TNAZ)/*N*-NITROSO-3,3-DINITROAZETIDINE (ONDNAZ)

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**ABSTRACT**

The binary phase diagram for the 1,3,3-trinitroazetidine (**TNAZ**)/*N*-Nitroso-3,3-Dinitroazetidine (**ONDNAZ**) system has been predicted computationally and determined experimentally. Physical mixtures behave thermally like a simple binary eutectic system on the **TNAZ**-rich side of the eutectic composition, while transitioning to that of a linear solid solution system on the **ONDNAZ** side. Fused mixtures exhibit the thermal characteristics associated with a simple linear solid solution system. Experimental eutectic temperature/composition (°C/mol percent **TNAZ**) values determined by using physical and fused mixtures are 83.4 ± 0.1 °C/58.4 to 63.0 and 82.3 ± 0.04 °C/60.1 to 64.8, respectively.



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## INTRODUCTION

1,3,3-Trinitroazetidine (**TNAZ**), a powerful and thermally stable energetic material, was first prepared by Archibald and co-workers in 1990[1] and has been investigated extensively at this laboratory in both the neat state and in binary eutectic systems. In particular, **TNAZ** mixtures with pentaerythritol tetranitrate (**PETN**), 2,4,6-trinitrotoluene (**TNT**), 1,3,5-trinitrobenzene (**TNB**) and *N*-methyl-*p*-nitroaniline (**MNA**) have been characterized for explosive performance and thermal/shock sensitivity.[2, 3, 4 and 5] In addition, **TNAZ**-based binary eutectic systems with 1,3-Dinitro-3-(1',3'-dinitroazetidin-3'-yl)azetidine (**TNDAZ**), **TNT**, *N*-Acetyl-3,3-dinitroazetidine (**ADNAZ**) and **TNB** have been characterized by using differential scanning calorimetry (DSC) and hot stage microscopy (HSM).[6, 7, 8 and 9]

It has been shown that **TNAZ** exists in at least two polymorphic modifications, one stable (**TNAZ I**) under ambient conditions and one unstable (**TNAZ II**), and that the former is more dense than the latter.[6] Crystal density increases with the spontaneous transition from **TNAZ** II to I resulting in a dendritic structure with characteristic macro-shrinkage cracks. These shrinkage cracks, which are distributed irregularly throughout a cast billet of pure **TNAZ**, are believed to cause low bulk density. It is this latter condition that led to the major research effort to find a **TNAZ**-based binary eutectic system that would eliminate the tendency to form randomly distributed macro-shrinkage cracks during the solidification process.

## EXPERIMENTAL

### Phase Diagram Calculation

Liquidus temperatures associated with this binary eutectic system were computationally derived by solving equation (1),

$$R\ln x = \Delta H_{fus}(-1/T + 1/T_o) \qquad (1)$$

where T is the melting point (K) of the eutectic composition, $T_o$, $\Delta H_{fus}$ and x are the melting point (K), heat of fusion (cal $mol^{-1}$) and mol fraction of component A or B, respectively, and R is the gas constant (1.987 calories $K^{-1}$ $mol^{-1}$). Experimental melting points, determined by DSC heating operations on mixtures of the stable polymorphs of both components, were used for comparison with their corresponding calculated values.

### Thermal Characterization

#### a. Differential Scanning Calorimetry (DSC)

**ONDNAZ** and selected **TNAZ/ONDNAZ** mixtures were thermally characterized by using a TA Instruments Dual Differential Scanning Calorimeter, Model 912, equipped with a 2100 Thermal Analyzer Data System. Standard aluminum sample pans and lids, TA Instruments Part Nos. 072492 and 073191, were used for all melting operations carried out by using the standard Dual Sample DSC (DSDSC) cell.

Lids were inverted to minimize free volume over the sample. An upper temperature limit of 105 °C and a sample weight not exceeding 2.0 mg were used to eliminate leakage from the sample pans. Heating operations were started at 30 °C.

At least two melting operations were carried out on all mixtures at a heating rate of 1 °C/min. Cooling operations were either uncontrolled or accomplished at approximately 5 °C/min by using ice/water as a cooling medium. Peak temperatures are reported for all endothermic and exothermic processes. Mixtures were prepared by grinding weighed portions of dry energetic materials in an agate mortar with a glass pestle for at least a 5-minute time period to ensure homogeneity. The DSC was calibrated by using indium metal as a temperature and calorimetric standard.



b. Hot Stage Microscopy (HSM)

Two HSM experiments were carried out by using a Mettler Hot Stage, Model FP 82, equipped with a FP 80 Central Processor. All observations were made with a Leitz Orthoplan Universal Largefield microscope equipped with a polarizing condenser and high-resolution video system, Javelin Smart Camera, Model JE3762DSP, which was operated at shutter speeds of 1/250 or 1/500 s. The video system is also equipped with a FOR-A video timer, Model VTG-55. All video data were obtained through a Leitz NPL 10X 0.20P lens (150x) at a heating rate of 1 °C/min. The sample was cooled at a rate of 5 °C/min to approximately 45 °C where the cooling rate is not controlled. The temperature at which the last crystal melts is reported as the liquidus temperature.

### Energetic Components

**TNAZ** was acquired from Aerojet Corporation and purified by crash-precipitation from a hot ethanol solution into ice and water and dried under vacuum. **ONDNAZ** was acquired from Los Alamos National Laboratory and used as received.[10] Analyses by high performance liquid chromatography showed **TNAZ** and **ONDNAZ** to be 97.8 and 97.2 percent pure, respectively.



## RESULTS

### Thermal Characterization

#### a. Thermal Properties of ONDNAZ and TNAZ

The melting point and heat of fusion of **ONDNAZ**, 102.4 ± 0.05 °C and 5.978 ± 0.119 kcal/mol, respectively (lit. mp 102.2 °C)[10], were obtained by DSC heating operations at 1 °C/min. No polymorphic modifications were observed. The melting point and heat of fusion observed for **TNAZ** were 99.7 ± 0.1 °C and 6.607 ± 0.079 kcal/mol, respectively.[6]

b. Calculated Phase Diagram

The calculated melting point and composition of the eutectic in this binary system are 72.6 °C and 49.8 mol percent **TNAZ**, respectively. The composition values and associated liquidus temperatures used to construct the calculated phase diagram are shown in Table 1.

Table 1. Mol Percent **TNAZ**/Calculated Temperatures Used to Construct the **TNAZ/ONDNAZ** Phase Diagram

| Mol Percent **TNAZ** | Temperature (°C) **TNAZ/ONDNAZ** |
|---|---|
| 0 | 102.4 |
| 5.0 | 100.0 |
| 9.2 | 97.9 |
| 15.0 | 94.9 |
| 18.6 | 93.0 |
| 25.0 | 89.4 |
| 28.3 | 87.4 |
| 30.0 | 86.4 |
| 35.0 | 83.2 |
| 37.9 | 81.3 |
| 39.5 | 80.2 |
| 42.9 | 77.8 |
| 45.0 | 76.3 |
| 47.8 | 74.2 |
| 49.8 | 72.6[1] |
| 55.0 | 76.3 |
| 57.9 | 78.2 |
| 60.0 | 79.5 |
| 63.0 | 81.3 |
| 65.0 | 82.5 |
| 68.1 | 84.3 |
| 70.0 | 85.4 |
| 76.5 | 88.8 |
| 78.6 | 89.9 |
| 83.9 | 92.5 |
| 89.2 | 95.0 |
| 94.6 | 97.4 |
| 100.0 | 99.7 |

1. Eutectic composition.

## C. DSC Characterization of **TNAZ/ONDNAZ** Mixtures

Initial melting operations, carried out on fifteen freshly ground mixtures of **TNAZ** and **ONDNAZ**, yielded a consistent endothermic event at an average temperature of 83.4 ± 0.1 °C that was observed only between 28.3 and 94.6 mol percent **TNAZ**. This event is believed to be associated with eutectic melting. No endothermic processes were observed below this temperature. Endothermic processes associated with **TNAZ** liquidus temperatures are characterized by a primary endothermic peak followed by a shoulder or tail. Temperatures associated with these events fall along two trendlines, 1 ($R^2$=0.997) and 2 ($R^2$=0.991), that are positioned on either side of that calculated (theoretical) by using equation (1). The trendline ($R^2$=0.998) through the experimental **ONDNAZ** liquidus temperatures is slightly convex-shaped and positioned well above the calculated liquidus curve. Four additional endothermic events, believed to be associated with **ONDNAZ** solidus temperatures, were observed between 9.2 and 35.0 mol percent **TNAZ**. Experimental temperatures from melting operations on physical mixtures are shown in Table 2 and graphically in Figure 1. Also shown in Figure 1 is the calculated temperature/composition diagram.

Table 2. Endothermic Peak Temperatures for Initial DSC Melting Operations with **TNAZ/ONDNAZ** Mixtures (1 °C/min)

| Mol Percent TNAZ | Temperature (°C) | | | |
|---|---|---|---|---|
| | Eutectic | TNAZ | ONDNAZ | ONDNAZ Solidus |
| 100.0 | | 99.8 | | |
| 94.6 | 83.1 | 97.9/96.2 | | |
| 89.2 | 83.2 | 95.8/93.8 | | |
| 83.9 | 83.4 | 93.8/90.9 | | |
| 78.6 | 83.4 | 91.6/88.5 | | |
| 76.5 | 83.5 | /87.5 | | |
| 68.1 | 83.4 | 85.6/ | | |
| 63.0 | 83.6[1] | | | |
| 57.9 | 83.4[2] | | | |
| 47.8 | 83.5 | | 87.0 | |
| 42.9 | 83.6 | | 88.0 | |
| 37.9 | 83.5 | | 89.9 | |
| 35.0 | 83.4 | | 91.2 | 89.0 |
| 28.3 | 83.4 | | 93.2 | 88.6 |
| 18.6 | | | 96.2 | 91.4 |
| 9.2 | | | 99.0 | 97.9 |
| 0 | | | 102.4 | |

1. Unsymmetrical endothermic curve (with tail).
2. Symmetrical endothermic curve eutectic composition.

Remelting of samples obtained by freezing of the molten mixtures from the initial DSC melting operations does not significantly affect the liquidus temperatures associated with **ONDNAZ**. The **TNAZ** liquidus temperatures, on the other hand, have changed from two distinct groupings into a single group that lies in close proximity to the trendline through the calculated liquidus temperatures. The eutectic melting temperature also shifted to an average value of 82.3 ± 0.04 °C and was only observed between 47.8 and 76.5 mol percent **TNAZ**. All experimental temperatures from remelting operations are shown in Table 3 and graphically in Figure 2. Also included in Figure 2 is the calculated temperature/composition diagram. Solidus temperatures extend from the neat materials to the positions marked *a* and *b*.

Table 3. Endothermic Peak Temperatures Associated with Melting Processes for All DSC Remelting Operations with **TNAZ/ONDNAZ** Mixtures

| Mol Percent | Temperature (°C) | | | | |
|---|---|---|---|---|---|
| | | **TNAZ** | | **ONDNAZ** | |
| **TNAZ** | Eutectic | Liquidus | Solidus | Liquidus | Solidus |
| 100.0 | | 99.8 | 99.8 | | |
| 94.6 | | 96.3 | | | |
| 89.2 | | 94.2 | 91.6 | | |
| 83.9 | | 91.7 | 87.8 | | |
| 78.6 | | 89.8/88.6 | 83.8 | | |
| 76.5 | 82.2 | 87.0 | | | |
| 68.1 | 82.3 | 84.7/83.7 | | | |
| 63.0 | 82.4 | | | | |
| 57.9 | 82.2 | | | 83.4 | |
| 47.8 | 82.2 | | | 86.5 | 83.0/82.6 |
| 42.9 | | | | 88.6/87.3 | 84.2 |
| 37.9 | | | | 89.8 | 87.0 |
| 35.0 | | | | 91.4 | 88.8 |
| 28.3 | | | | 93.6 | 91.2 |
| 18.6 | | | | 96.6 | 95.4 |
| 9.2 | | | | 99.4 | 99.0 |
| 0 | | | | 102.4 | 102.4 |

d. HSM Characterization of **TNAZ/ONDNAZ** Fused Mixtures

HSM melting operations were carried out at a heating rate of 1 °C/min on single thin crystalline films of mixtures containing 42.9 and 78.6 mol percent **TNAZ** that had previously been melted on a hot plate. Color changes were observed over the temperature range 76.3-77.3 °C for the former and at 81 °C for the latter. These color changes are believed to be associated with solid solution compositional changes. A liquidus temperature was also observed at 90.6 °C for the former. Eutectic melting was not observed.

f. TNAZ Behavior in Binary Mixtures

As stated in a previous manuscript[9], the liquidus temperatures from mixtures with **ONDNAZ** fall close to the trendline through those calculated for **TNAZ** (Figure 3). This apparent near ideal behavior was similar to that observed from its mixtures with **TNDAZ**[6], whereas its binary mixtures with **TNT**[7], **ADNAZ**[8], and **TNB**[9] clearly behaved non-ideally. In its mixtures with the latter three materials, its melting temperatures are in close proximity to a single trendline fit to the combined data points ($R^2$=0.990) and fall below the trendline through the calculated liquidus temperatures.

## DISCUSSION

No polymorphic modifications were observed for **ONDNAZ** during multiple DSC or HSM heating operations with the neat compound. It was previously shown that **TNAZ** exists in at least two polymorphic modifications, one stable (**TNAZ** I) and one unstable (**TNAZ** II). There were no observations to suggest that **TNAZ** polymorphism affected the nature of the temperature/composition diagram.

The temperature/composition diagram constructed from initial DSC melting operations is consistent with that expected from a simple binary eutectic system on the **TNAZ**-rich side of the eutectic composition. The **TNAZ** liquidus temperatures, in all but one case observed as a broad endothermic peak accompanied by a shoulder or tail, were recorded as two distinct temperature series that lie on either side of the calculated liquidus temperature trendline. These trendlines, designated 1, 2, and the calculated line in Figure 1, intersect the line projected through the average eutectic temperature at 63.5, 70.4 and 66.5 mol percent **TNAZ**, respectively. The **ONDNAZ**-side of the eutectic composition, on the other hand, appears to be in transition from that of a simple eutectic to a solid solution system. Endothermic processes believed to be associated with both liquidus and solidus temperatures were observed, the latter only between 9.2 and 35.0 mol percent **TNAZ**. The trendline through the **ONDNAZ** liquidus temperatures ($R^2$=0.998) intersects the line through the average eutectic temperature at 58.6 mol percent **TNAZ**. These trendline intersections suggest the eutectic composition falls within the compositional range 58.6 to 63.5 mol percent **TNAZ**. This is consistent with the DSC findings in that the mixture with 57.9 mol percent **TNAZ** yielded a symmetrical endothermic curve suggesting this mixture was at or very near the eutectic compositional value. The mixture with 63.0 mol percent **TNAZ** yielded an unsymmetrical endothermic curve (slight tail) suggesting it was rich in the **TNAZ** component. The eutectic mixture observed in these melting operations with physical mixtures is presumed to be composed of the pure components.

The temperature/composition diagram constructed from DSC remelting operations is representative of a simple linear solid solution system. The mixtures between *a* and *b* (approximately 47.8 and 76.5 mol percent **TNAZ**, respectively) in Figure 2 behave like a simple binary eutectic system in which the eutectic mixture is composed of the saturated solutions, *a* and *b*, instead of the pure components, **TNAZ** and **ONDNAZ**. The trendlines through the **ONDNAZ** liquidus temperatures ($R^2$=0.995) and those calculated for **TNAZ** intersect the line representing the average eutectic melting temperature at 60.1 and 64.8 mol percent **TNAZ**, respectively. The average melting temperature of the eutectic composition is 82.3 ± 0.04 °C with the eutectic composition believed to be in the range 60.1 to 64.8 mol percent **TNAZ** (lit. mp 82.6 °C and 54 mol percent **TNAZ**).[11] In fact, the composition with 63.0 mol percent **TNAZ** yielded a single, nearly symmetrical endotherm at 82.4 °C suggesting this mixture is *near or at* the eutectic composition. Compositions between pure **ONDNAZ** and *a* and pure **TNAZ** and *b* behave like simple linear solid solution systems under equilibrium conditions.



The similarity of the non-ideal melting characteristics associated with **TNAZ**, when in binary mixtures with **TNT**, **ADNAZ** and **TNB**, is believed to be associated with component interaction. These interactions, affecting the **TNAZ** component in a similar manner, lower its apparent heat of fusion, thus resulting in experimental melting temperatures below those calculated by using its measured heat of fusion. A best fit, linear trendline through these combined data points has an R-squared value of 0.990. When in binary mixtures with **ONDNAZ** and with **TNDAZ**, a similar interaction is not observed and, in fact, the melting temperatures tend to follow the calculated melting curve fairly closely.

## CONCLUSIONS

A temperature/composition diagram for the **TNAZ/ONDNAZ** binary system has been predicted computationally by using measured heats of fusion and melting points obtained from DSC melting operations on the neat components. Similarly, experimental diagrams have been determined for both physical and fused binary mixtures. The diagram constructed from physical mixture data is consistent with that of a simple binary eutectic system on the **TNAZ**-rich side of the eutectic composition and that of a system transitioning to a simple linear solid solution system on the **ONDNAZ** side. The eutectic melting temperature and approximate composition associated with physical mixtures are 83.4 ± 0.1 °C and 58.4 to 63.0 mol percent **TNAZ**. Eutectic melting is observed only at **TNAZ** concentrations at or greater than 28.3 mol percent. Fused mixtures exhibit the characteristics of a simple linear solid solution system with eutectic melting (82.3 ± 0.04 °C) observed between approximately 47.8 and 78.6 mol percent **TNAZ**. The eutectic composition is believed to fall in the range 60.1 to 64.8 mol percent **TNAZ**.

## ACKNOWLEDGMENTS

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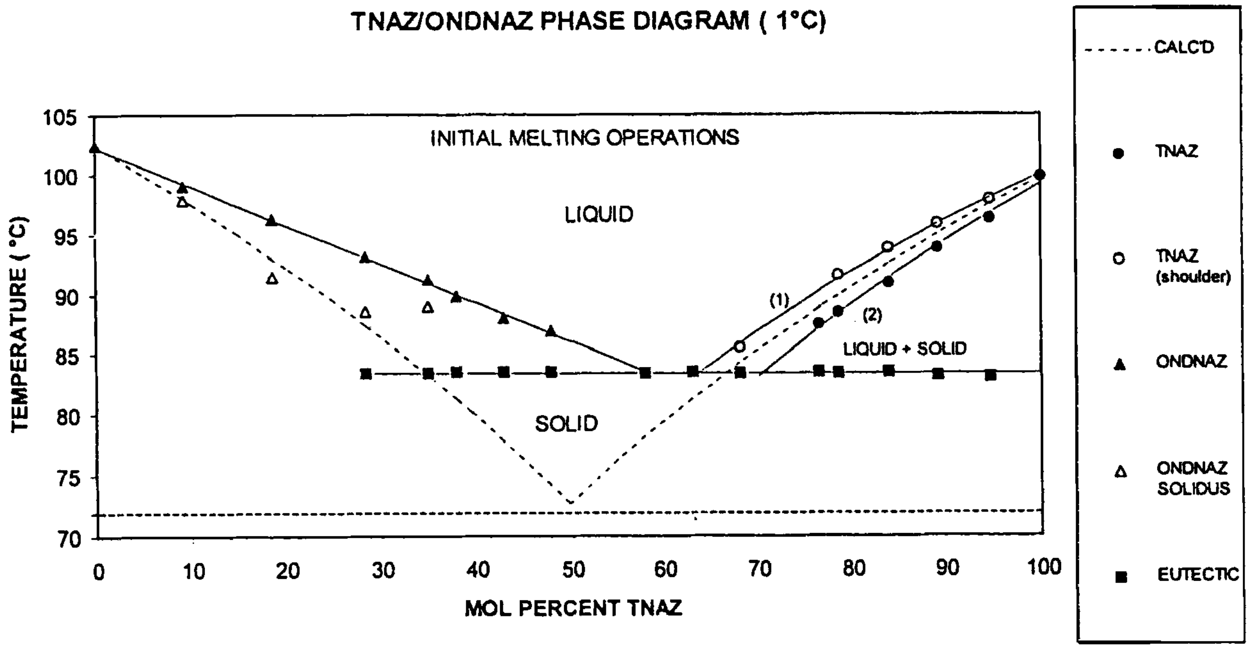


FIGURE 1.
Experimental temperature/composition diagram for the TNAZ/TNB binary system from initial DSC melting operations.

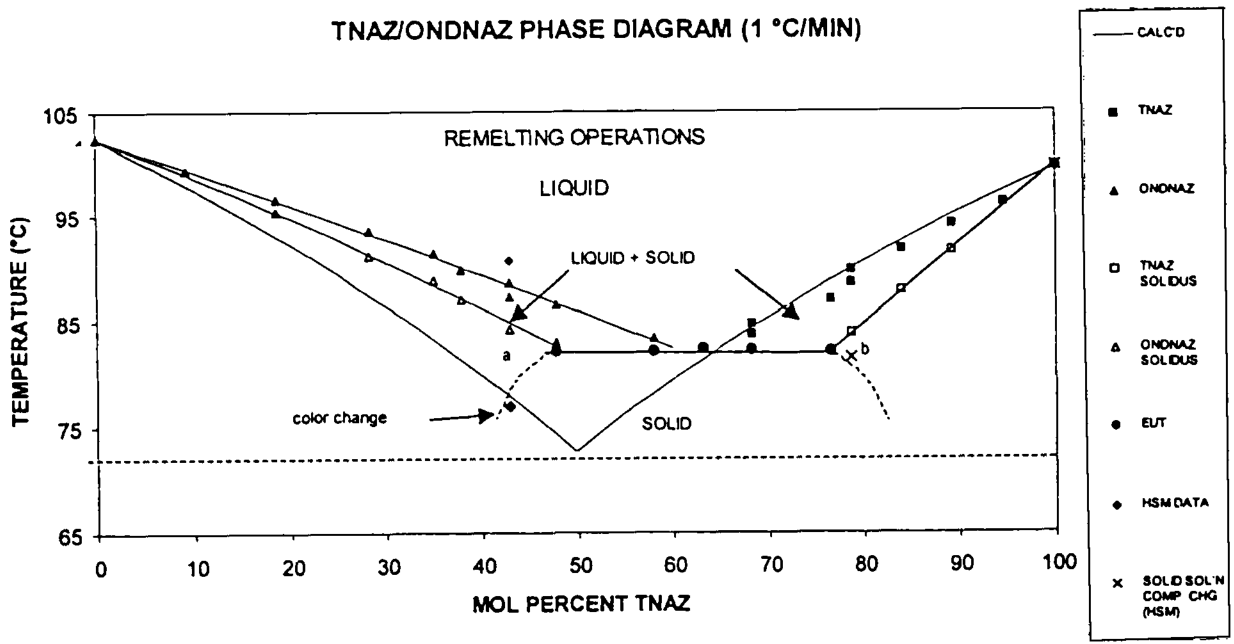


FIGURE 2.
Experimental temperature/composition diagram for the **TNAZ/TNB** binary system from DSC remelting operations.

## TNAZ MELTING TEMPERATURES IN BINARY MIXTURES

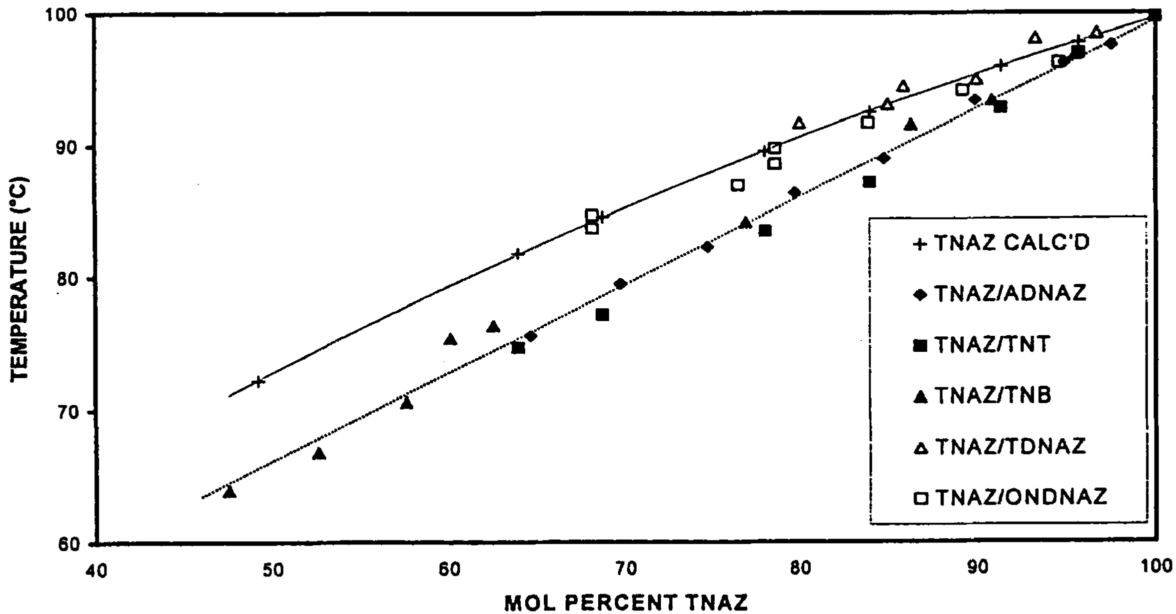


FIGURE 3.
Graphical representation of calculated and experimental **TNAZ** melting temperatures when in binary mixtures with **ADNAZ**, **TNT**, **TNB**, **TDNAZ** and **ONDNAZ**