The shock sensitivities of nitromethane/methanol mixtures

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Abstract. Dilution of liquid explosives with “inert” solvents have been shown previously to affect a degradation in the detonation performance properties of the explosive, and result in a rapid increase in the critical diameter with increasing diluent. To date, the shock sensitivities of liquid explosive-diluent mixtures have not been measured. In this work, we describe the results of a series of gas gun-driven plate impact experiments on nitromethane (NM)-methanol (MeOH) solutions of several concentrations, using in situ electromagnetic gauging to measure the initial shock state (Hugoniot) of the mixture, as well as the overtake-time-to-detonation (Pop-plot). Surprisingly, the shock sensitivities did not fall off dramatically with increasing MeOH concentration. In fact, at some concentrations MeOH appears to sensitize NM, relative to neat NM.

1. Introduction
Understanding the concentration limits at which explosive mixtures will detonate is of critical importance for the safe handling and transportation of explosives and related chemical commodities. It is also of interest for the fundamental detonation physics of how diluents influence the shock sensitivity and resultant reactive flow, including detonation velocities and pressures, chemical reaction zone dynamics, and detonation wave stabilities. Quantifying the “detonability” limits of explosive mixtures is challenging because the critical diameter ($d_c$) rapidly increases with increasing diluent [1, 2]. A compelling alternative is “infinite diameter” 1-D gas gun-driven plate impact experiments with in situ measurements of the shock and reactive wave profiles to look for evidence of initiation as a function of concentration. Here “infinite diameter” implies that the shock and reactive flow are unperturbed by confinement or rarefaction waves on the time and length scales of the measurement.

Nitromethane (NM, CH$_3$NO$_2$) is a well-characterized liquid explosive. Its reactant and product equations of state (EOS), initiation sensitivity, and detonation performance characteristics have been extensively investigated, and multiple studies have further elucidated how the sensitivity of NM can be altered by chemical or physical means [3-11]. The detonation properties of NM diluted with solvents such as acetone or methanol have also been reported previously [1-2]. In particular, several works have illustrated the role of dilution on the formation of cellular structures in detonating NM/solvent solutions [1,2]. In the present work, we investigate the shock initiation sensitivities of NM:MeOH solutions with concentrations ranging from 90:10 to 65:35 (by weight). The objectives of this study were to: 1) assess changes in the shock sensitivity of NM:MeOH as a function of diluent using gas gun-driven plate impact to initiate explosive mixtures in an “infinite diameter,” 1-D configuration; 2) obtain insights into the initiation mechanisms by in situ measurements of shock and...
reactive wave profiles using embedded electromagnetic gauging techniques; and 3) make quantitative comparisons of the measured detonation parameters with thermochemical predictions.

2. Experimental
Nitromethane was purchased from Sigma-Aldrich (99+%) and used without further purification.

2.1. Plate impact experiments
Gas gun-driven plate impact experiments were performed using a two-stage, 50 mm bore (launch tube) light gas gun at Los Alamos National Laboratory [14]. Kel-F 81 (polychlorotrifluoroethylene) impactors were contained in Lexan projectiles and launched at velocities ranging from 2.804 to 3.204 km/s into instrumented targets containing the NM:MeOH solution. Embedded electromagnetic gauges were used as the principal diagnostic for measuring shock and reactive wave profiles in NM:MeOH solutions, as described previously [14-16]. The gauges provide in situ particle velocity profiles at up to 10 Lagrangian positions, allowing for determination of both the initial, unreacted shocked state (Hugoniot locus) and overtake time-to-detonation. The gauges used at LANL are thin (5 µm) Al foil elements sandwiched between two FEP-Teflon membranes, forming a gauge package approximately ~60 µm thick. This gauge package is inserted on a 30° angle in a LANL-designed liquid cell consisting of a PMMA body, and Kel-F 81 front, positioning the gauges from ~1 to 7 mm into the liquid sample [14,15]. A single ~0.94 cm-long single gauge element, called a “stirrup” gauge, was affixed to the front of the liquid cell in contact with the NM:MeOH solution, and was used to obtain the shock input condition. Projectile velocities were measured using an optical interrupt system mounted at the exit interface of the launch tube, and errors in projectile velocity are typically < 0.1%.

2.2. Physical properties and calculated detonation parameters.
Several of the physical properties of NM:MeOH solutions were measured for comparison with values reported by Koldunov et al. [2]. The ambient pressure bulk sound velocity was measured using a pulse-echo method, driven by a Panametrics HV pulser/receiver model #5058PR acoustic transducer. Densities of the solutions were measured using a 25 mL liquid pycnometer, and refractive indices were measured using an optical refractometer. Selected properties of NM:MeOH mixtures are reported in table 1. The Cheetah 6.0 thermochemical code [17] was used to calculate initial densities, detonation velocities, Chapman-Jouget (CJ) pressures (\(P_{\text{CJ}}\)) and particle velocities (\(u_{\text{CJ}}\)) as a function of concentration, and are also presented in table 1. The calculated detonation velocities were corrected (Corr. Det. Vel.) by scaling the predicted detonation velocity to the measured infinite diameter detonation velocity for neat NM, table 1.

3. Results and Discussion
Gas gun-driven plate impact experiments were used to generate sustained shock inputs to NM:MeOH solutions at a range of concentrations from 90:10 to 65:35 NM:MeOH. In all cases, the experiments were performed to impart a shock with sufficient input stress (pressure) to initiate the mixture, starting with 90:10 NM:MeOH, and working down in wt% NM along the shot series. The experimental conditions, measured initial shock states (shock input conditions), overtake times to detonation, and detonation velocities are summarized in table 2.

Figure 1 shows particle velocity wave profiles measured in shots 2s-503 (90:10), 2s-599 (80:20), 2s-607 (70:30), and 2s-720 (65:35). The first wave profile, at \(t = 0\) µs, is obtained from the response of the stirrup gauge at the shock input interface to the NM:MeOH solution. All of the solutions exhibited shock initiation mechanisms with the salient features of the modified homogeneous initiation mechanism: thermal explosion, reactive wave build-up and overtake of the initial shock, and formation of an overdriven detonation at overtake, which settles down to a steady detonation [9].
Table 1. Physical properties and calculated detonation parameters of NM:MeOH solutions.

| NM:MeOH Wt% | Density (g/cm³) | Bulk sound velocity (mm/µs) | Refractive index (nD) | Calc. Det. Veloc. (km/s) | Corr. Det. Veloc. (km/s) | Calc. PCJ (Gpa) | Calc. U_p, CJ (mm/µs) |
|-------------|----------------|----------------------------|----------------------|-------------------------|--------------------------|----------------|------------------------|
| 100:0       | 1.140/1.140    | 1.317                      | 1.3802 (23.8 °C)     | 6.45                    | 6.26                     | 12.8 (12.5)   | 1.74 (1.75)            |
| 90:10       | 1.092/1.092    | 1.273                      | 1.3743 (24.0 °C)     | 6.19                    | 5.99                     | 11.4          | 1.69                   |
| 80:20       | 1.048/1.045    | 1.240                      | 1.3802 (23.8 °C)     | 5.93                    | 5.74                     | 9.9           | 1.59                   |
| 70:30       | 1.007/1.004    | 1.215                      | 1.3802 (23.8 °C)     | 5.68                    | 5.49                     | 8.6           | 1.51                   |
| 60:40       | 0.969/0.966    | 1.198                      | 1.3802 (23.8 °C)     | 5.44                    | 5.25                     | 7.5           | 1.42                   |

Figure 1. Particle velocity wave profiles measured during the shock-to-detonation transition of NM:MeOH solutions with concentrations ranging from 90:10 to 65:35 NM:MeOH. The shot numbers in the Figures correspond with the experiments summarized in table 2.
A t-x diagram illustrating the homogeneous initiation mechanism is shown in figure 2, along with measured shock and reactive wave arrival time-distance points obtained in shot 2s-720, 65:35 NM:MeOH with \( P_{in} = 8.2 \) GPa and \( t_D = 2.1 \) µs. Even for this highly diluted solution, the initiation mechanism remains the same as observed in neat liquid explosives (NM, >97.5% H\(_2\)O\(_2\)/H\(_2\)O, etc.) [9, 10, 13], and shock initiation to detonation is observed at 2.10 µs. Overtake times as a function of shock input condition are plotted as Pop-plots [18] in figure 3, and reported in table 2. Figure 3 also shows Pop-plots for neat NM [4-9], NM with 5 wt% diethylenetriamine (DETA) [11], >97.5 wt% H\(_2\)O\(_2\)/H\(_2\)O [13] for comparison. From the Pop-plots, the different liquid explosives appear to have similar state (P,T) sensitivities (e.g. similar slopes in the Pop-plot), and the relative sensitivities of different liquid explosives can be discerned. Surprisingly, dilution of NM with MeOH appears to have minor effects on shock sensitivity relative to neat NM, even at concentrations down to 65:35 NM:MeOH, table 2. In fact, MeOH appears to sensitize NM at 70:30 NM:MeOH concentration. The measured overtake time to detonation in 70:30 NM:MeOH is shorter than that of neat NM at the same shock input condition.

Figure 2. (left) Time-distance (t-x) diagram illustrating the features of the initiation of homogeneous explosives [3,10-13]. (right) Response of the particle velocity gauges, and three shock trackers recorded in shot 2s-720, 65:35 NM:MeOH with \( P_{in} = 8.2 \) GPa, \( t_D = 2.1 \) µs. A superdetonation was observed just prior to overtake in this experiment.

Dilution perturbs the shock initiation and resultant reactive flow of the NM:MeOH solutions relative to NM in several ways. As observed in the wave profiles for 65:35 NM:MeOH in figure 1, the reactive wave is temporally broader compared with the profiles for higher NM concentrations. While the shock sensitivity does not dramatically fall off with increasing wt% MeOH, the detonation performance parameters are predicted to change substantially. Decreases in the CJ pressure and detonation velocity with increasing diluent are predicted by Cheetah, and consistent with the measured increases in critical diameter and reported detonation velocities by Koldunov [2]. In our experiments, the measured detonation velocities remain high, table 2, with increasing MeOH content, but this may be a consequence of measurement at early times following turnover when the wave is still settling down, and support near or above CJ. We do observe that a regime is reached in the series in which the shock input condition necessary for overtake between 0.2-2 µs is above the CJ condition. In this case, the detonation wave following turnover is supported above CJ, and the flow becomes perturbed. This is clearly observed in shot 2s-607 in figure 1. In this experiment, the shock input pressure was 9.3 GPa. The predicted CJ condition is \( P_{CJ} = 8.6 \) GPa, or \( u_{CJ} = 1.51 \) mm/µs. As can be seen in the profiles, the support from the impactor is \( u_p \approx 1.87 \) mm/µs, and above \( u_{CJ} \). Evidence of the perturbed
flow after turnover can be observed in gauges 6-9 ($t \approx 0.9-1.3$ $\mu$s). The flat top to the profiles is interpreted as the gauge element averaging over a complex wave structure.

In conclusion, the shock sensitivities of NM:MeOH solutions with concentrations from 90:10 to 65:35 NM:MeOH have been measured using sustained shock input conditions, with \textit{in situ} measurements of the reactive flow. All of the solutions were observed to initiate by a homogeneous initiation mechanism, at shock input conditions relevant to initiation of NM. Surprisingly, the shock sensitivities do not change substantially with increasing MeOH content. We have also supported the detonation above CJ, and observed evidence of instabilities as a result.

### Table 2. Summary of unreacted Hugoniot states, and overtake times-to-detonation for NM:MeOH solutions. Also included are the early-time detonation velocities measured in the experiments. The input shock pressure was calculated from the measured interface particle velocity, initial density, and projectile velocity by impedance matching to Kel-F 81 ($\rho_0 = 2.14$, $c_0 = 1.989$, $s = 1.763$).

| Shot #  | NM:MeOH wt% | $V_{proj}$ (km/s) | Initial density (g/cm$^3$) | $u_p$ (mm/$\mu$s) | $U_s$ (mm/$\mu$s) | $P_{in}$ (GPa) | $t_D$ ($\mu$s) | Meas. Det. Vel. (km/s) | Supported above CJ |
|---------|--------------|-------------------|-----------------------------|-------------------|-------------------|---------------|---------------|---------------------|-------------------|
| 2s-502  | 88.8:11.2    | 3.204             | 1.092                       | 1.900             | 5.735             | 11.9          | $\sim0.16$    | 6.10                | Yes               |
| 2s-503  | 90:10        | 2.880             | 1.092                       | 1.720             | 5.332             | 10.0          | 0.80          | 6.68                | Close             |
| 2s-599  | 80:20        | 2.850             | 1.045                       | 1.738             | 5.184             | 9.4           | 1.08          | N/A                 | Close             |
| 2s-607  | 70:30        | 2.974             | 1.004                       | 1.867             | 4.933             | 9.3           | 0.61          | 5.95                | Yes               |
| 2s-720  | 65:35        | 2.871             | 0.985                       | 1.777             | 4.778             | 8.2           | 2.10          | N/A                 | Close             |
| 2s-721  | 67.33        | 2.804             | 0.994                       | 1.765             | 4.844             | 8.5           | $\geq2.5$     | N/A                 | Close             |

**Figure 3.** Shock input pressure (GPa) vs. overtake time to detonation ($\mu$s) (Pop-plot) illustrating shock initiation sensitivities of neat NM [11-16], NM with 5 wt% diethylenetriamine (DETA) [18], >97.5 wt% H$_2$O$_2$/H$_2$O [18], and NM:MeOH solutions from this study.
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