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# Detonation Properties of Nitromethane/Diethylenetriamine Solution

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**Abstract.** The results of the experimental determination of the detonation parameters of nitromethane (NM) with diethylenetriamine (DETA) solution are presented in this work. With the using of a laser interferometer VISAR the stability of detonation waves, the detonation velocity and the reaction time at the concentration of DETA from 0 to 60 weight percentage were investigated. It is shown that the stability of detonation waves is retained up to 25% DETA, at that the characteristic reaction time is reduced by about half at the addition of several percentage of the sensitizer to NM and then remains almost constant. The increase of the detonation velocity in the vicinity of the small, about 0.1%, concentrations of sensitizer is recorded.

Small additions of amines significantly affect the detonation properties of nitromethane  $\text{CH}_3\text{NO}_2$  (NM): reduce the critical diameter [1-3], the pressure of the shock-wave initiation, expand the concentration range of detonation for mixture of NM with inert diluents [4], qualitatively change the character of the flow in the reaction zone, resulting almost to the disappearance of the Von Neumann spike [5]. This is due to a sharp increase of the chemical rate of reaction of NM at addition of amines. Possible reasons of this effect are analyzed in detail in several papers [2, 6-9]. When we talk about low concentrations of sensitizers, hundredths of a percent, a noticeable influence on the thermodynamic properties of nitromethane it doesn't provide. At the same time, at high concentrations the amines can be regarded as inert diluents, which reduce the heat of the explosion of mixture, change its physical properties and, therefore, must significantly change the detonation parameters up to impossibility of the propagation of detonation waves.

The aim of this work is an experimental study of detonation phenomena in mixtures of nitromethane with diethylenetriamine  $(\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{NH}$  (DETA) in a wide range of concentrations. The focus is on studying of the influence of the sensitizer on the stability of one-dimensional detonation, width of the chemical reaction zone and the detonation velocity.

## EXPERIMENTAL SCHEME

The scheme of experiments is shown in the inset of Fig.1. NM with an initial density of  $1.14 \text{ g/cm}^3$  [7, 8] and DETA with an initial density of  $0.954 \text{ g/cm}^3$  [9] were used in the experiments. Mixtures of NM/DETA were prepared immediately before the experiments. The HE charge was placed in shells of different internal diameter and material (4). The detonation was initiated by a pressed charge of HE (1). A laser beam was reflected from 7-400  $\mu\text{m}$  Al foil (3) which was placed between the end of the charge and the water window (2). The shock wave transit time in 7  $\mu\text{m}$  foil is less than 2 ns, which is less than the time resolution of the interferometer VISAR, which was used for recording the velocity. Therefore, the experimental data shows the velocity of movement of the HE/water boundary. The interferometer constant is equal to 305 m/s, resulting in velocity measurements which are accurate to  $\pm 10 \text{ m/s}$ . At the same time in each experiment, the detonation velocity,  $D$ , was measured using ionization gauges (5). The second time-reference point was the interferometer signal, which recorded the arrival of the detonation wave at the boundary of the HE and window. The accuracy of the detonation velocity measurements was no worse than 0.2%, or  $\pm 0.01 \text{ km/s}$ .

Figure 1 shows typical velocity profiles which were recorded at the HE/water boundary for mixture of NM/DETA at the use of 7  $\mu\text{m}$  foil. The velocity change over time for NM (curve 1) corresponds to the classical model of detonation: after the shock jump and formation of the Von Neumann spike the velocity is observed to decrease through the reaction zone. The transition from the reaction zone to the unloading wave is smooth, so that it is impossible to uniquely choose the Chapman-Jouguet point on the profile. This question has been considered in detail in [11] where it was shown that the reaction time was 50 ns. Small additions of DETA fundamentally change the distribution of parameters in the reaction zone. This is most clearly observed in the velocity growth after the shock jump and the formation of a flat maximum in the vicinity of 10 ns, what, for example, demonstrates curve 2 in Fig.1, corresponding to 0.5 weight percentage of DETA. In detail the influence

of small concentrations of DETA on NM was investigated in [5]. Figure 1 shows that this unusual behavior of the velocity profile in the reaction zone remains with increasing of DETA concentration up to 25%. This is due to the reaction of HE in the shock wave front, and because of this the maximum pressure moves deeper into the reaction zone and its amplitude is lower than the value corresponding to the intersection of the Rayleigh line and the unreacted Hugoniot [5, 12].

## THE INSTABILITY OF DETONATION WAVES

One-dimensional flow in the detonation waves is unstable to small perturbations, if the ratio of the activation energy to the temperature behind the shock jump exceeds a critical value [13-19]. The result is the formation of a complex cellular structure of the detonation wave. The recording of such flow by interferometric technique is complicated, if the velocity oscillations aren't smoothed at the propagation of the shock wave through the foil, which reflects the laser beam (3 in the inset in Fig.1). However, even at high instability it is possible to obtain the records that not only contain information about the average distribution of parameters, but also can tell about the character size of the inhomogeneities. For example, the velocity profiles in Fig.1, obtained with 7  $\mu\text{m}$  Al foil, are smooth, without oscillations, which could be associated with the formation of the cellular structure of the detonation front. This means that the one-dimensional detonation wave in nitromethane and its mixtures with DETA is stable up to a concentration of the sensitizer about 25%. A similar conclusion about the stability of detonation in NM was made in [5, 11]. Note that we are talking about the instability of one-dimensional flow, which takes place at the absence of the influence of the boundaries. Instability at the edge of the charge, resulting in the appearance of waves of reaction failure was studied in detail by the authors [18] and in this paper is not considered.

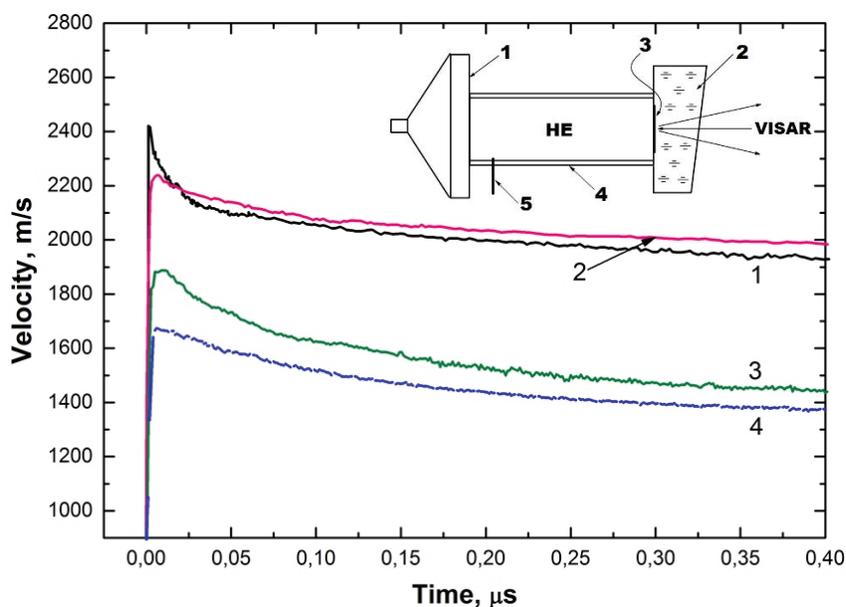


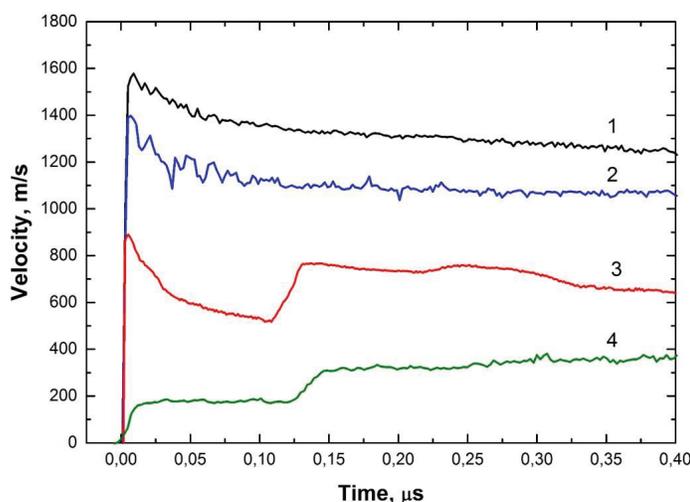
FIGURE 1. Velocity profiles for NM - 1 and NM/DETA solution (2 – 99,5/0,5, 3 – 85/15, 4 – 75/25). Internal diameter of the shell: 1, 2 – polyethylene Ø36 mm; 3 – steel Ø30 mm; 4 – brass Ø27 mm.

The stability of detonation waves in mixtures of NM/DETA at such high dilution, reaching 25%, is not typical for the addition of inert, not detonating additives. For example, it is sufficiently about one percent of acetone or methanol for losing of the detonation front stability [11]. The first signs of instability of detonation for NM/DETA appear at 30% of DETA. In the velocity profiles it looks like the character oscillations (Fig.2). The increasing of the amount of DETA up to 40% results in an rise of the oscillations amplitude (curve 2 in Fig.2). Since heterogeneities on the front are not smoothed after transition of the shock wave through the 7  $\mu\text{m}$  foil, this means that their amplitude of the order of the thickness of the foil.

Further increase of the DETA concentration causes so strong rise of the oscillations amplitude that it is almost impossible to obtain reproducible results with the use of 7  $\mu\text{m}$  Al foil for reflection of the laser beam. Nevertheless, the use of thick aluminum foil, up to 400 microns, at propagation through which the oscillation amplitude decreases, allows to record the velocity profiles that provide information about the averaged distribution of parameters in the unstable detonation waves. Previously, such a registration scheme allowed to

obtain reproducible results for the mixture of NM/methanol 65/35, which was close to the limit concentration of detonation [11]. The data obtained in a similar way for the mixture of NM/DETA 42/58, are shown in Fig.2 (curve 3). It is seen that the averaged velocity profile corresponds to the classical model of detonation: after the shock jump and formation of the Von Neumann spike the velocity is observed to decrease through the reaction zone. The rise of velocity, which is observed after about 100 ns, is due to the circulation of waves of compression and rarefaction through 400  $\mu\text{m}$  Al foil [19]. The absence of high-frequency oscillations of velocity in curve 3 means that the amplitude of the oscillations is much less than 400 microns. At the same time, it is more than 10 microns, since at use of 7  $\mu\text{m}$  foil it is impossible to record the process. Therefore the longitudinal size of the inhomogeneities of the order of 100 microns.

At DETA concentration of 62 weight percentage the detonation in the mixture attenuates and on the boundary with water the compression pulse, whose amplitude after passing of 150 mm from the initiation point isn't higher than 1 GPa, is recorded (curve 4 in Fig.2). This means that the critical concentration of DETA, at which a mixture of NM/DETA doesn't detonate, is about 60%.



**FIGURE 2.** Velocity profiles for NM/DETA solution: (1 – 70/30; 2 – 60/40; 3 – 42/58; 4 – 38/62). Internal diameter of the shell: 1, 2 – steel Ø36 mm; 3, 4 – brass Ø27 mm.

## REACTION TIME

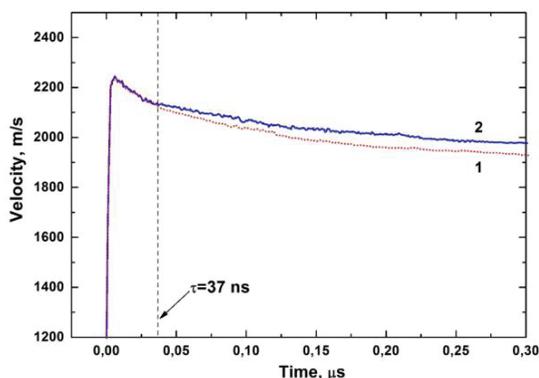
The difficulty in determination of the Chapman-Jouguet point in liquid HE is due to the absence of any peculiarities on the velocity profile at the transition from the reaction zone to the unloading wave. Nevertheless, the problem of determination of the width of the chemical reaction zone, despite the noted difficulties, fundamentally can be solved unambiguously. For example, it is sufficient to conduct experiments with charges of different diameters. If the diameter is much greater than the critical one, the flow in the reaction zone remains constant while the velocity gradient in the unloading wave depends on the diameter. Also it can be used another configuration of experiment, for example, changing of the compressibility of the shell material, or the conditions of detonation initiation. It is important to conduct the experiment such that the flow in the reaction zone coincides, but in the unloading wave diverges in the different configurations.

Previously, this method was used for determination of the reaction time in nitromethane, which was equal to 50 ns [11]. It can be expected a significant influence of DETA on the width of the reaction zone, since, as noted above, the small additions of DETA sharply reduce the critical diameter of nitromethane, which, according to the model [20], is proportional to the reaction time. It should be noted also that the reduction of the critical diameter allows the use in the experiments of relatively small shells, but of different diameters, and it will not influence the flow in the reaction zone.

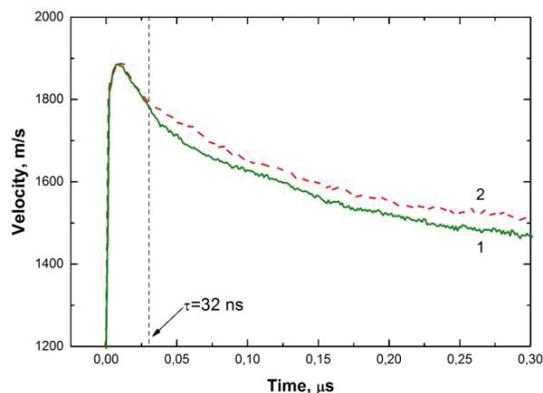
Figure 3 shows the velocity profiles for the mixture NM/DETA 99.5/0.5, which was placed in shells of foamed plastic with internal diameters of 20 mm (curve 1) and 30 mm (curve 2) and a wall thickness of 10 mm. The compressibility of foamed plastic with a density of 0.2  $\text{g}/\text{cm}^3$  is an order of magnitude higher than that of nitromethane, therefore the charges may be considered unconfined. After the shock jump for the first approximately 35 ns, the velocities in the experiments 1 and 2 coincide, within the accuracy of measurement. This is the area of the reaction zone, wherein the distribution of the parameters doesn't depend on the charge

diameter. A noticeable difference due to the effect of the charge diameter on the change of the parameters in the unloading wave begins after 38 ns. Therefore, the characteristic reaction time,  $\tau$ , is equal to  $37 \pm 2$  ns.

Similar experiments were conducted at DETA concentrations of 1, 2, 15 and 25%. For NM/DETA 99/1 and 98/2 the reaction times within the error are the same and equal to  $30 \pm 2$  ns. Further increase of the amount of DETA results in a slight increase of the width of the reaction zone. As an example, Fig. 4 and 5 show the results of experiments at a concentration of DETA of 15% and 25%. For both concentrations in the experiments, which results are presented by curves 1, polypropylene shells with internal diameter of 36 mm were used. Curves 2 show the results of experiments, where shells were made from steel with internal diameter of 30 mm (Fig.4) and brass 27 mm (Fig.5). The difference between the obtained velocity profiles begins at  $32 \pm 2$  ns and  $34 \pm 2$  ns for mixtures of NM/DETA 85/15 and 75/25, respectively. It should be noted that the discrepancy is caused not so much by changing of diameters of the shells as the material from which they are made.

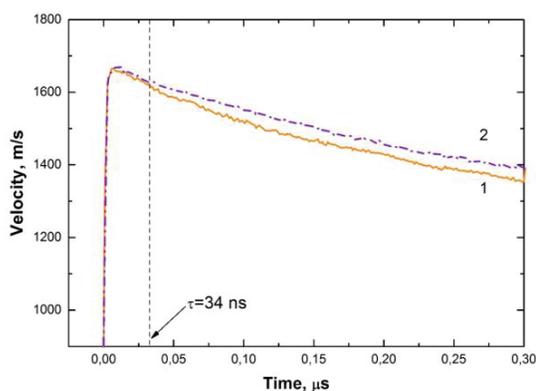


**FIGURE 3.** Velocity profiles for NM/DETA 99,5/0,5 solution for different diameters of tubes from foam plastic (1 –  $\varnothing$ 20 mm, 2 -  $\varnothing$ 30 mm).

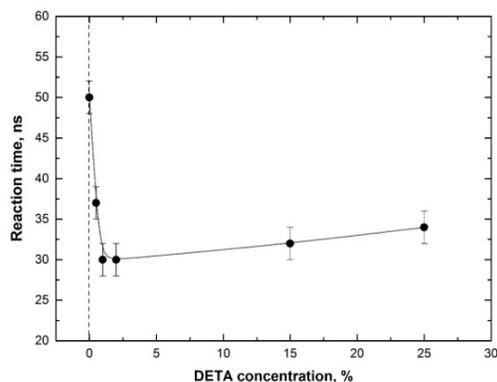


**FIGURE 4.** Velocity profiles for NM/DETA 85/15 solution for different diameters and materials of tubes: 1 – polyethylene  $\varnothing$ 36 mm; 2 - steel  $\varnothing$ 30 mm.

The experimental results are summarized in Fig.6. As it was expected, the reaction time decreases with the increasing of DETA concentration. Moreover, a noticeable decrease of  $\tau$ , from 50 to 30 ns, occurs in the concentration range from 0 to 1%, and at the further increase of the amount of the sensitizer up to 25% a width of the reaction zone is almost unchanged. At higher concentration of DETA, as shown above, the detonation front becomes unstable, and due to this it was impossible to perform measurements with satisfactory accuracy.



**FIGURE 5.** Velocity profiles for NM/DETA 75/25 solution for different diameters and materials of tubes: 1 - polyethylene  $\varnothing$ 36 mm; 2 – brass  $\varnothing$ 27 mm.



**FIGURE 6.** The dependence of reaction time of NM/DETA solution on concentration of DETA.

## DETONATION VELOCITY

In each experiment the detonation velocity of the investigated mixture was measured. Figure 7 shows the results of the experiments (black points) and their approximation (straight line). There are three areas on the obtained dependence. At low concentrations (inset in Fig.7) the detonation velocity increases, reaches a

maximum at 0.2% and returns to value, close to the neat nitromethane, at about 0.3% of DETA. Moreover, the increase of velocity is greater than 1% and well reproduced in the experiments.

In the second area, at the change of DETA concentration from 0.5 to 10%, the detonation velocity monotonically decreases by approximately 1%. At further increase of the concentration a much more rapid decline of  $D$  is observed and at approaching to the critical concentration of  $D$  it tends to about 5 km/s. Such difficult character of the change of detonation velocity is quite atypical at dilution of nitromethane with inert, not detonating liquid. Typically, almost a linear decline of  $D$  with increasing of the sensitizer concentration is observed [21,22].

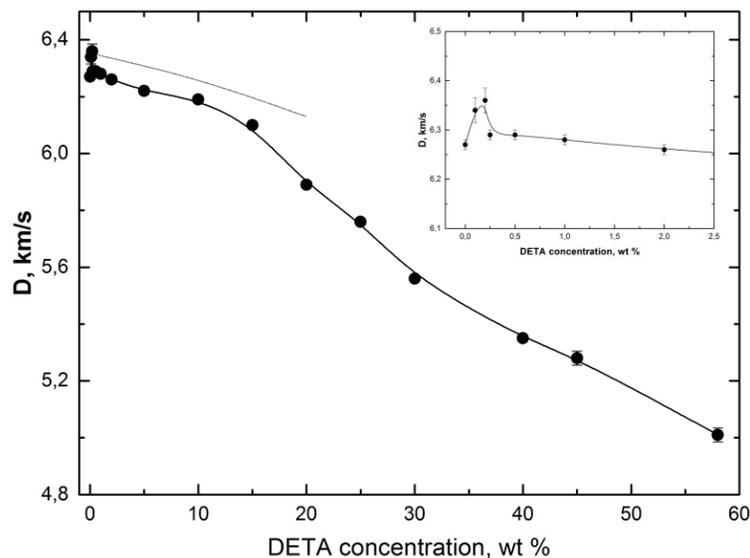


FIGURE 7. The dependence of detonation velocity of NM/DETA solution on DETA concentration.

## DISCUSSION

Obtained results show that even at high concentrations of DETA in a mixture with nitromethane the diethylenetriamine retains the properties of the sensitizer. First of all, the stability of detonation waves up to 25% of DETA is observed. The stability of the flow is determined, first of all, by rate of the chemical reaction, and investigation of the reaction zone width shows that dilution of nitromethane reduces the characteristic reaction time by a factor of 1.5 in the entire region of the stability of detonation wave (Fig.6). As noted above, we talk about the stability of one-dimensional flow, which is realized at the absence of the influence of boundaries. We don't consider in this paper how DETA influences the instability of flow at the edge of charge, the consequence of which there are waves of the failure of reaction in nitromethane [18]. Nevertheless, it should be noted that the additions of DETA result in stabilization of the flow at the edge of the charge too, and as result the detonation front in nitromethane becomes completely stable.

The second feature of the mixture of NM/DETA is the high value of the maximum concentration of diluent, 60%, above which the detonation is impossible. Probably, this is also due to the high rate of decomposition of nitromethane at the addition of a sensitizer even at high dilution. It is known [18] that a necessary condition for the possibility of propagation of the detonation wave is a positive reaction heat at constant pressure and volume. Under this condition, everything is determined by the value of the critical diameter. The increase of the reaction rate of NM at the addition of DETA reduces the critical diameter and the detonation wave can be observed in laboratory conditions even when concentration of nitromethane in the mixture is less than 50%.

It is unexpectedly, that there is a maximum of the detonation velocity in the dependence on the concentration of DETA for small values of the sensitizer (Fig.7). Thermodynamic calculation on the scheme [23], shown in Fig.7 by the dashed line, predicts monotonous decrease of the detonation velocity, without any peculiarities. It is also impossible to explain the presence of the maximum by change in the kinetics of decomposition of NM at small additions of DETA. Perhaps the reason is the change of the composition of the explosion products, what affects their equation of state, and causes an increase in  $D$ . But then it is not clear why this happens in such a narrow range of DETA concentrations. Attention should be paid to the fact of slight reduction of detonation velocity in the concentration range from 0.5 to 10% of DETA, and it is in a good agreement with thermodynamic calculation. However, at further increase of the sensitizer concentration the discrepancy between the

experimental and calculated values of D increases. In particular, the calculation on the scheme [23] doesn't predict more rapid decline of the detonation velocity at concentrations above 15%.

Thus, as a result of conducted investigations it was found a strong influence of diethylenetriamine on the stability of one-dimensional detonation, the width of the chemical reaction zone and the detonation velocity. It was shown that the stability of the detonation waves was retained up to 25% of DETA, at that the characteristic reaction time was reduced by at least a factor of two at the addition of several percentage of the sensitizer and then remained almost constant.

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