The stabilization of unstable detonation waves for the mixture of nitromethane/methanol

2015 J. Phys.: Conf. Ser. 653 012053

(http://iopscience.iop.org/1742-6596/653/1/012053)

The stabilization of unstable detonation waves for the mixture of nitromethane/methanol

A V Utkin[1,2], S A Koldunov[1], V M Mochalova[1,2], S I Torunov[1] and S M Lapin[3]

[1] Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Academician Semenov Avenue 1, Chernogolovka, Moscow Region 142432, Russia
[2] Tomsk State University, Lenina Avenue 36, Tomsk 634050, Russia
[3] Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119991, Russia

E-mail: `roxete20000@hotmail.com`

Abstract. Using a laser interferometer VISAR the measurements of the particle velocity profiles in detonation waves for nitromethane/methanol mixtures with additions of a sensitizer diethylenetriamine were conducted. It is shown that the detonation front in a mixture of nitromethane/methanol is unstable and sensitizer is an effective method for the flow stabilization. If the diluent concentration is less than 10%, the detonation front is stabilized by adding of 1% diethylenetriamine. At higher concentrations of methanol, the sensitizer does not reject instability, but the amplitude of oscillations decreases in several times. An increase of the limit concentration of methanol at the addition of diethylenetriamine to the mixture was found.

The dilution of liquid high explosives (HE) by inert additives affects not only the detonation parameters of the mixture, but also results in a qualitative change in the detonation waves structure. Most clearly this is shown in the loss of the detonation stability and the existence of a critical concentration of diluent, above which the mixture does not detonate. The appearance and development of flow instability in the detonation waves is primarily determined by the kinetics of chemical reactions [1–3], the rate of which is usually reduced by dilution of liquid HE by inert additives. The small additions of sensitizers result in the opposite effect—an increase of the reaction rate, which should have a stabilizing effect on the flow instability. Therefore, triple mixtures of HE-inert diluent-sensitizer allow for the change in a wide range of the HE properties and the investigation of the influence of the thermodynamics and kinetics on the structure and the critical conditions of the detonation waves propagation.

The aim of this work is an experimental study of the possibility of the unstable detonation waves stabilization in a mixtures of nitromethane (NM) with methanol (M) by additives of sensitizer of diethylenetriamine $(CH_2CH_2NH_2)_2NH$ (DETA). It is known that in a neat nitromethane the one-dimensional detonation front is stable [4], while methanol additive [4], which is an inert diluent, results in the loss of stability and the formation of a cellular structure. In [5] it was shown that small additions of DETA qualitatively changed the character of the flow in the reaction zone, leading to almost disappearance of von Neumann spike. This is due to a sharp increase of the chemical reaction rate of nitromethane in a detonation conditions at the addition of amines. Therefore, it can be expected the stabilizing effect of DETA on the detonation in a mixture of NM/M. The character of influence of the sensitizer on the value of

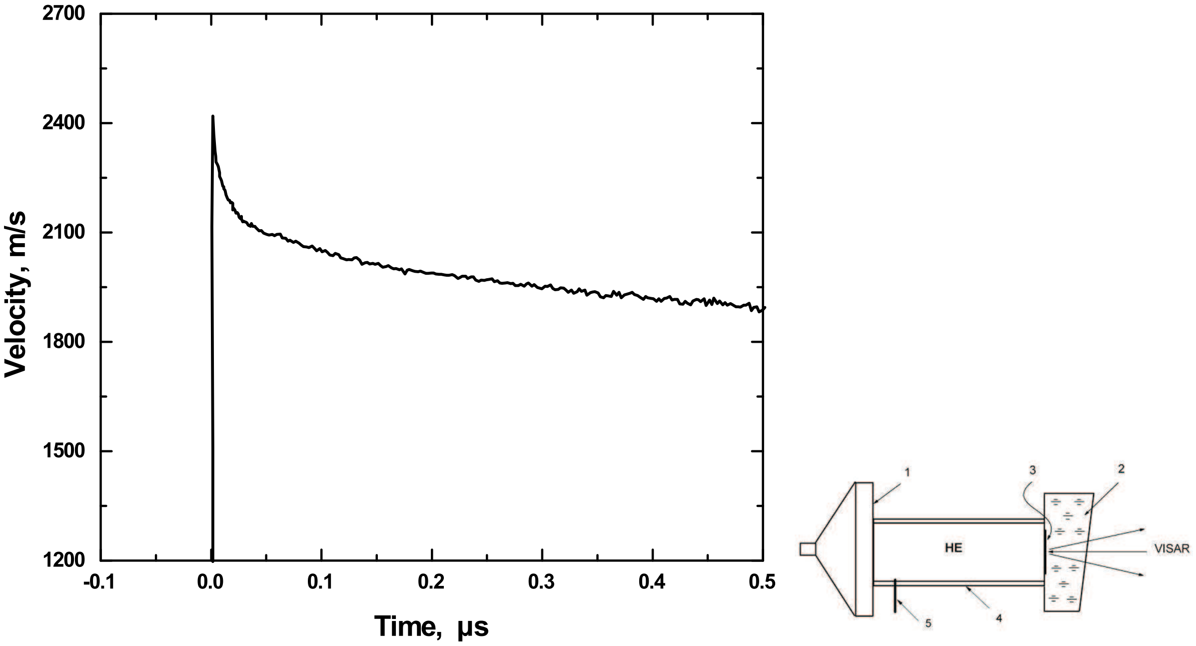

Figure 1. Velocity profile of the nitromethane–water boundary. Polypropylene shell. The scheme of the experiment is on the right-hand side.

the limit concentration of methanol is less obvious, which is also the subject of study of this work.

The scheme of experiments is shown on the right-hand side of figure 1. The HE charge was placed in shells of different material—polypropylene or steel (4). The internal diameter of shell was 36 mm, the wall thickness—2 mm, the length of charge was 150 mm. The detonation was initiated by a pressed charge of HE (1). A laser beam was reflected from 7–400 μm Al foil (3) which was placed between the end of the charge and the water window (2). The particle velocity profile was recorded by the laser interferometer VISAR at the Al foil/window boundary. Therefore, the experimental data show the velocity of movement of the HE/water boundary. 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 0.3%.

HE mixtures were prepared immediately before the experiments. An initial density and refractive index of NM at 20°C were equal to 1.137 g/cm^3 and 1.3816, respectively. An initial density of DETA was 0.954 g/cm^3, for methanol it was equal to 0.790 g/cm^3. Typical velocity profile recorded at the HE/water boundary for NM is shown in figure 1. The foil thickness was 7 μm. After the shock jump, the velocity decrease is observed with the formation of the von Neumann spike in the reaction zone with time duration of 50 ns [4]. As previously noted [4], the dependence of velocity on time is smooth, without any oscillations that could be associated with the formation of the cellular structure of the detonation front. This means that the one-dimensional detonation wave in NM is steady.

The situation changes radically when nitromethane is diluted by inert additives. As a rule, it is enough at the order of one percent of the diluent for the loss of stability of the detonation front. Figure 2 shows the experimental results for a mixture of NM/M 90/10 (the dependence 1). The addition of 10 weight % of methanol results in the drop of detonation parameters, and

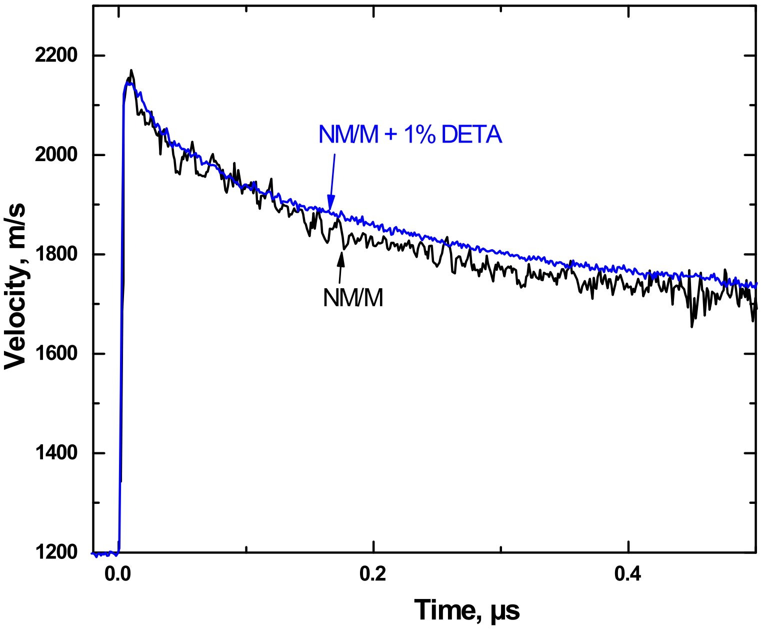

Figure 2. Velocity profiles for the NM/methanol 90/10 and NM/methanol 90/10 + 1% DETA solutions. Polypropylene shell.

as a result, in loss of stability that causes oscillations on the recorded velocity profiles. Since the disturbances do not attenuate during the transition of the shock wave through the 7 microns Al foil, this means that the amplitude of instabilities has a value comparable to the thickness of the foil, i.e. about 10 microns. It should be noted that it remains small in comparison with the chemical reaction zone, the width of which is 200 μm [4]. The transverse dimension of the pulsation cannot be estimated on the basis of the received data, but we know that usually it is an order of magnitude greater than the amplitude of oscillations [6, 7].

At addition of 1 weight % of DETA to the mixture oscillations disappear, and the velocity profile becomes smooth (dependence 2 in figure 2), i.e. the detonation front of mixture is stabilized.

With the increase of methanol concentration up to 20% the oscillations amplitude rises sharply, however, the results are reproduced even with 7 micron aluminum foil (dependence 1 in figure 3). The addition of 10% DETA practically stabilizes the flow in the unloading wave, at times exceeding of 0.1 microseconds (dependence 2 in figure 3). Since all velocity profiles W in figure 3 are superposed on each other, the dependence 2 is down to 150 m/s and the dependence 3 is down to 300 m/s for visibility. However, in the reaction zone, the instability remains and, instead of von Neumann spike, the area of oscillating parameters is recorded. The instability of the detonation wave remains by the addition of 20% DETA, but the character of the flow changes significantly: the amplitude of the oscillations in the reaction zone is reduced and clearly observed von Neumann spike is observed on the averaged velocity profile (dependence 3 in figure 3).

The character sizes of the cellular structure at the methanol concentration above 20% increase up to several hundred microns, it allows observing of the pulsations of unstable detonation front in the NM/M mixture. To obtain such information the experiments, using a streak camera, were conducted. The images, obtained from the streak camera, have shown, however, that the DETA addition results in the loss of transparency of the mixture and the impossibility of registration of

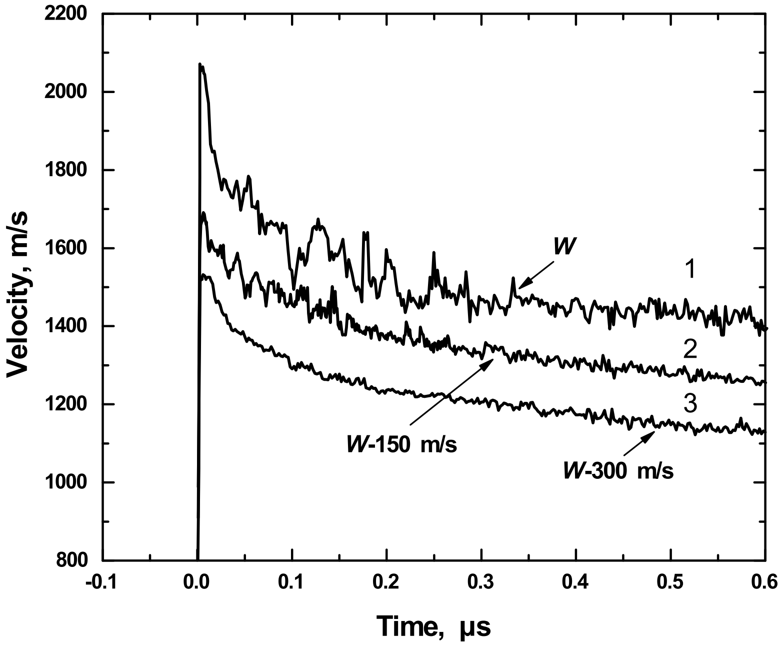

Figure 3. Velocity profiles on the boundary with water window: 1—NM/M 80/20, 2—NM/M 80/20 + 10% DETA, 3—NM/M 80/20 + 20% DETA. Steel shell.

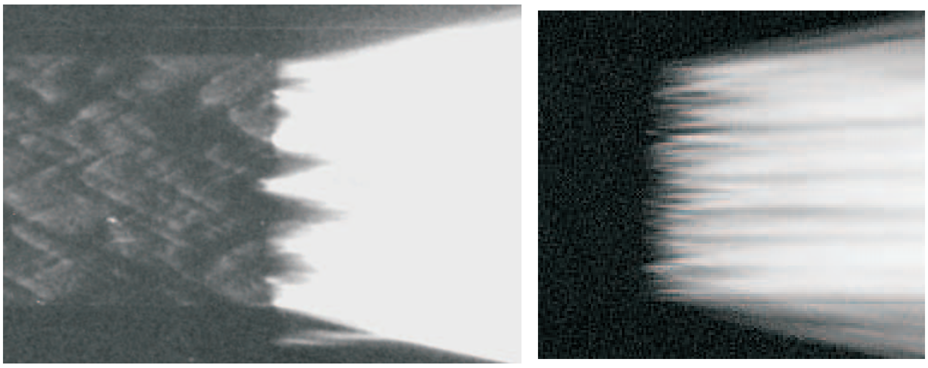

Figure 4. The streak images of the exit of the detonation wave on the free surface for the mixture of NM/M 66/34 without DETA (left) and with 2% DETA (right). Steel shell with the internal diameter of 28 mm and the length of 300 mm.

the detonation front glow at its propagation in the depth of the sample. Therefore, conclusions about the detonation wave structure can be made only on the basis of the observation of the process of its exit on the free surface of the liquid. The images, demonstrating the effect of the transparency loss and changes in the structure of the detonation front in the NM/M mixture 66/34 with the addition of 2% DETA are shown in figure 4. In the mixture of NM/M (figure 4, left) at the wave propagation through a liquid, the character for unstable detonation non-uniform glow of the front is observed [6]. At the time of the exit of the wave on the free surface, the brightness of the glow increases dramatically, and the character size of the inhomogeneities remains unchanged. At addition of DETA (figure 4, right) the detonation wave propagation inside the liquid cannot be observed, and glow is recorded only when wave exits on

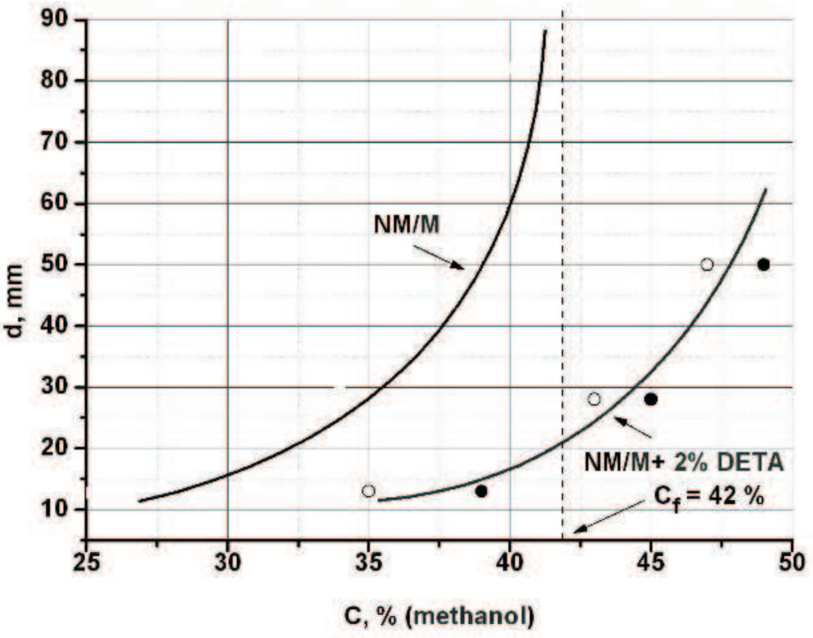

Figure 5. The influence of addition of DETA on the critical diameter of detonation for NM/M solution.

the free surface. Difficulties with the registration of the detonation front glow are caused by the diethylenetriamine chemical activity, leading to the formation of the aci-ion, which facilitates the transformation of the nitromethane molecule under shock-wave action [8]. Also one of the results of the interaction between the sensitizer and nitromethane is a change in its optical properties, which results in the screening of the detonation front glow.

Despite the impossibility of observation of the detonation front structure directly into the liquid at the addition of DETA, the registration of moment of the appearance on the free surface of glow products allows making a conclusion about the changes in the detonation process, caused by the presence of diethylenetriamine in the mixture. In the images from the streak camera it is seen, in particular, that the character size of the inhomogeneities decreased by about an order of magnitude at the addition of 2% DETA.

The dilution of nitromethane with methanol, as with the others inert liquids, results in an increase of the critical diameter of detonation. At a certain limit concentration of the diluent, depending on the nature of the inert liquid, the critical diameter converges to infinity, which means the loss of the detonation ability of the mixture. The limit concentration of methanol C_f in the mixture of NM/M was determined by the authors [9] and it is approximately equal to 40%. Because even small amounts of DETA, about hundredths of percent, essentially reduce the critical diameter of nitromethane [10], then a noticeable influence of the amine on the limit concentration of methanol can be expected.

The results of the critical diameter determination of the mixtures, obtained in the same conditions as without and with the addition of 2% DETA are shown in figure 5. The fact that the detonation took place was established mainly by the character of the steel shells fracture through the limit of the length filled with a fluid (up to 10–15 diameters), as well as the deformation of non-filled part of the shell with the length about 5 cm. Bright points correspond to the exit of

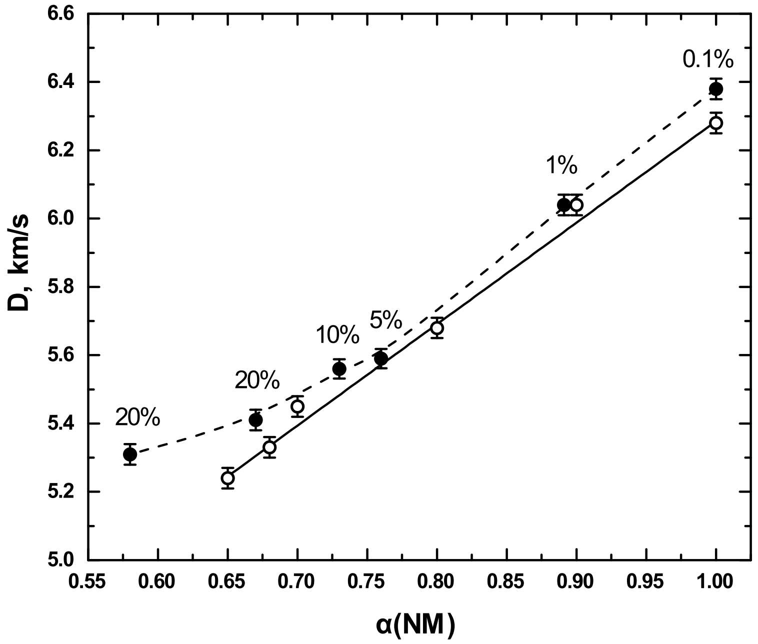

Figure 6. Dependence of detonation velocity on the nitromethane concentration α(NM) for the NM/M + DETA solution.

the detonation on the steady-state regime, the dark points—attenuation. It can be seen that the addition of 2% diethylenetriamine increases the limit concentration of methanol up to 48%, i.e. more than 10%. Of particular interest is the fact that mixtures, which cannot detonate in the absence of the sensitizer, acquire the ability to detonate.

Conditions of appearance of the detonation process in the NM/M + DETA solution depend on the diethylenetriamine content, the amount of which should vary in a certain range. Thus, the minimum required amount of DETA is in the range from a few tenths up to a few percent. And this amount is so smaller, as more the content of nitromethane in the initial mixture. The maximum content of DETA in the detonation-capable mixture reaches several tens of percent. The value of the maximum concentration is always less in a more diluted limit mixture, i.e. in the one, in which the initial percentage of nitromethane is smaller.

In each experiment in the investigated mixtures, the detonation velocity was measured. Figure 6 shows the dependence of the detonation velocity on the concentration of nitromethane in the mixture of NM/M + DETA. The solid line represents an approximation of dependence of the detonation velocity on the nitromethane concentration α for the mixture of NM/M: $D = 3.31 + 2.97\ \alpha$. Bright points, the results obtained in this work, which are in a good agreement with the data [9]. Black points—the detonation velocity values for the mixture of NM/M + DETA. Numbers above the black points indicate the values of weight concentrations of DETA in relation to the mixture of NM/M. It is notable that the DETA additions result in a slight increase in the detonation velocity of the mixture at the methanol concentration below the limit value, which is equal to 40%. A similar effect of a slight increase in the detonation velocity for nitromethane was observed early at low additions of the sensitizer, not exceeding 0.5% [5]. But the most surprising is that the decrease in the detonation velocity slows dramatically with the addition of 20% DETA in the mixture of NM/M 80/20 and 70/30, when the concentration of nitromethane is less than 67%.

Conducted investigations have shown that the sensitizer DETA has a stabilizing effect on an unstable detonation waves in the mixtures of NM/M: or completely rejects the instability, or significantly reduces the oscillations amplitude. This is due to a sharp increase in the rate of the chemical reaction of nitromethane at the addition of amines. Possible reasons for this effect are analyzed in detail in a number of works [8, 11–14]. From the viewpoint of the stability of the detonation wave, the important fact is that the amines reduce activation energy, stabilizing thus the flow. Destabilizing factor is the decrease of temperature in the reaction zone at increase of the concentration of an inert diluent. The mutual influence of these two factors determines the composition of mixtures with a stable detonation front. It should be emphasized that we are talking about the loss of stability of one-dimensional flow. The instability of the non-one-dimensional flow on the edge of the charge, leading to the appearance of waves of failure of reaction [6], is not considered in this paper.

The loss of the detonation front stability in general does not mean that the one-dimensional theory of detonation for averaged profiles does not work. At low oscillations amplitude, when the methanol concentration does not exceed of 10%, the particle velocity profiles have the form which is a typical for one-dimensional detonation with a distinct von Neumann spike in the reaction zone. The situation is not so obvious at higher concentrations of diluent, when the character size of the inhomogeneities is comparable to the width of the chemical reaction zone. As already noted, at 20% of methanol it is impossible to speak about any distribution of the parameters in the reaction zone. This is partly due to the recording scheme. Firstly, the use of 7 micron aluminum foil does not result in a significant smoothing of oscillation, when its amplitude is comparable to or greater than the thickness of the foil. Secondly, the size of the spot, to which the laser beam is focused on the surface of the foil, is approximately 100 microns, which is smaller than the transverse dimension of instabilities [7]. Therefore, at a highly developed instability the used method of recording, which is a local, does not allow getting information about the averaged velocity profile. Nevertheless, it is possible using a thick (400 μm) aluminum foil, at propagation through which the amplitude of the oscillations attenuates, and recorded velocity profiles give information about the average distribution of parameters in unstable detonation waves. Obtained results of measurements at a methanol concentration of 32% (dependence 1) and 35% (2 dependence) are shown in figure 7.

After the shock jump the velocity decrease at the foil-water boundary is observed, the duration and amplitude of which are determined by the parameters of von Neumann spike in the mixture of NM/M. The subsequent velocity increase after 100 ns is due to the circulation of compression and rarefaction waves in the 400 μm foil. At the propagation through the foil the oscillations of velocity are almost completely attenuate at the concentration of 32%, and the character length of von Neumann spike, which is more than 100 ns, can be estimated. At the concentration of 35%, which is close to the critical one, the velocity oscillations are so great that are not smoothed by 400 μm foil. However, the formation of von Neumann spike in this case is obvious.

The reduce of the reaction time for the mixtures of nitromethane with inert diluents at addition of DETA is likely the reason of increase of the limit concentration of methanol and deceleration of velocity drop D with the decrease of nitromethane concentration in the mixture. It is impossible to explain the character of changes in these values from the standpoint of thermodynamics, because DETA in this respect behaves like methanol. Therefore, the reason is probably in a change of the rate of decomposition of nitromethane at the addition of the sensitizer. Indeed, with the decrease of nitromethane concentration in the mixture of NM/M the reaction time increases, and in the result a part of HE does not react in the reaction zone and decomposed in the unloading wave. DETA reduces the reaction time and thereby facilitates to the increase of energy release directly in the reaction zone, which increases the limit concentration of methanol and decreases the velocity drop D with increase of the sensitizer concentration.

Thus, it was shown in the work that the sensitizer diethylenetriamine results in either the rejection of the instability of the detonation front in the mixtures of nitromethane with methanol, if the concentration of inert diluent is less than 10%, or in essential decrease of the amplitude

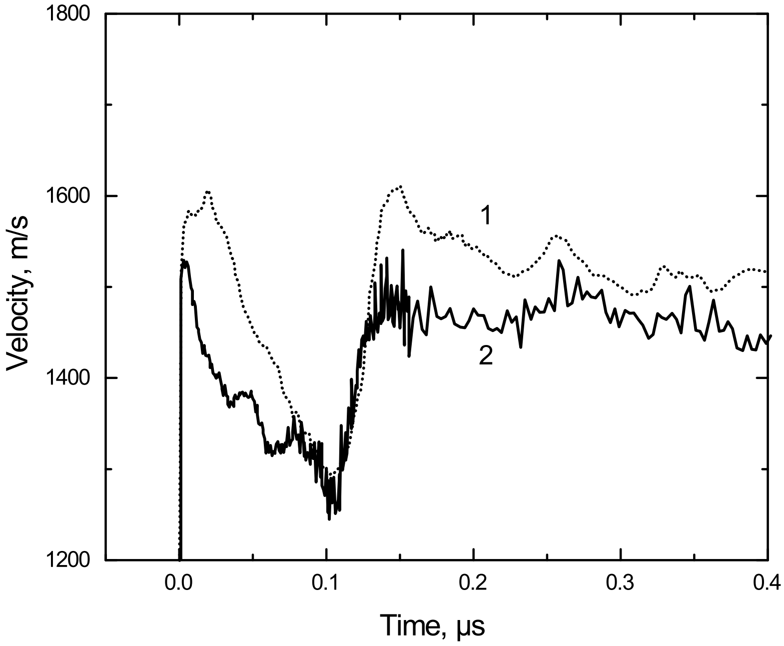

Figure 7. Velocity profiles on the boundary with water window: 1—NM/M 68/32; 2—NM/M 65/35. The foil thickness is 400 μm. Steel shell.

of oscillations at the higher concentrations of diluent.

Acknowledgments

This work was supported by Russian Foundation for Basic Research (project No. 15-03-07830).

References

[1] Schelkin K and Troshin Ya 1963 *Gas Dynamics of Combustion* (Moscow: Academy of Sciences USSR)
[2] Zaydel R 1961 *Dokl. Akad. Nauk SSSR* **136** 1142
[3] Aslanov S K, Budzirovskiy V N and Schelkin K I 1968 *Dokl. Akad. Nauk SSSR* **182** 53
[4] Utkin A V, Mochalova V M and Garanin V A 2012 *Combust. Explos. Shock Waves* **48** 350
[5] Utkin A V, Mochalova V M and Logvinenko A A 2013 *Combust. Explos. Shock Waves* **49** 478
[6] Dremin A, Savrov S, Trofimov V and Shvedov K 1970 *Detonation Waves in Condensed Matter* (Moscow: Nauka)
[7] Torunov S I, Kulish M I, Mochalova V M, Utkin A V and Yakushev V V 2013 *Russ. J. Phys. Chem.* B **7** 759
[8] Engelke R, Schiferl D, Storm C B and Earl W L 1988 *J. Phys. Chem.* **92** 6815
[9] Koldunov S A, Anan'in A V, Garanin V A, Sosikov V A and Torunov S I 2010 *Combust. Explos. Shock Waves* **46** 64
[10] Kondrikov B N, Kozak G D, Raikova M V and Starshinov A V 1977 *Dokl. Akad. Nauk SSSR* **233** 402
[11] Engelke R 1980 *Phys. Fluids* **23** 785
[12] Starshinov A V, Kondrikov B N, Kozak G D and Raikova M V 1977 *Chemical Physics of Combustion and Explosion. Detonation* (Chernogolovka: OIKhF AN SSSR) p 73
[13] Constantinou C P, Winey J M and Gupta Y M 1994 *Phys. Chem.* **98** 7767
[14] Gruzdkov Y A and Gupta Y M 1998 *J. Phys. Chem.* A **102** 2322