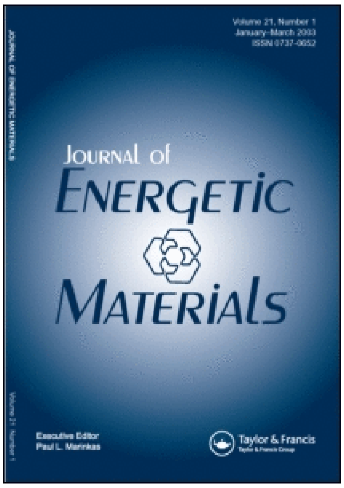

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Reducing Dangerous Effects of Unsymmetrical Dimethylhydrazine as a Liquid Propellant by Addition of Hydroxyethylhydrazine—Part I: Physical Properties

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Reducing Dangerous Effects of Unsymmetrical Dimethylhydrazine as a Liquid Propellant by Addition of Hydroxyethylhydrazine— Part I: Physical Properties

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In this work, the effect of low volatile hydroxyethylhydrazine (HEH) as a solute on unsymmetrical dimethylhydrazine (UDMH) has been studied in order to reduce harmful effects of UDMH vapors. Desirable physical properties of binary mixtures UDMH/HEH have been measured and compared to pure UDMH. These properties include boiling point, viscosity, density, and vapor pressure that are important for using binary mixtures of UDMH/HEH as less dangerous liquid propellants. Due to the formation of strong hydrogen bonding between UDMH and HEH, the volatility of UDMH has been reduced appreciably upon the addition of HEH. It is indicated that the measured physical properties may deviate significantly compared to

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corresponding predicted values. Binary mixtures of UDMH/HEH can also react spontaneously in contact with nitrogen tetroxide (NTO) and red fuming nitric acid (RFNA), so they can be called hypergolic propellants.

Keywords: green liquid propellant, hydroxyethylhydrazine, physical property, safety, UDMH

Introduction

Liquid propellants have some advantages such as high specific impulse and thrust levels as well as better thrust control compared with solid propellants [1]. They are commonly used in bipropellant systems for rocket launchers [1]. Computer codes or empirical methods can be used to evaluate their performance [2,3]. Conventional hydrazine derivatives including hydrazine, monomethylhydrazine (MMH), unsymmetrical dimethylhyrazine (UDMH), or their combinations belong to hypergolic propellants that can react spontaneously when in contact with suitable liquid oxidizers such as nitrogen tetroxide (NTO) [1]. These hydrazine derivatives have the advantages of being well-known and tested technology as well as versatile and reliable. Many hypergolic hydrazine derivatives–oxidizer combinations have the desirable properties of high energy density per unit mass and short ignition delays. For example, Salvador and Costa [1] have compared the performance of conventional hydrazine derivatives and their mixtures burning with NTO in a bipropellant rocket combustion chamber. Unfortunately, they are acutely toxic and suspected carcinogens; costly safety precautions and handling procedures are required [4].

Because UDMH has relatively high vapor pressure at room temperature, the most likely occupational exposure route of UDMH is inhalation. Hydroxyethylhydrazine (HEH) is a hydrazine derivative that can be used in pharmaceutical, agrochemical, polymer, and dye industries and also as a precursor in organic synthesis [5]. In this article, we will introduce HEH as a suitable hydrazine derivative with very low vapor pressure at room temperature, which can be combined with UDMH to reduce its occupational exposure. Some important physical properties including boiling point, viscosity, density, and vapor pressure of binary mixtures of UDMH/HEH have been measured and demonstrated. Suitable theoretical methods have also been used to predict these properties and compared to corresponding measured values. It will be shown that the presence of hydrogen bonding between UDMH and HEH is an important factor for deviation of the measured values from the predicted results.

Theory

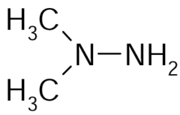
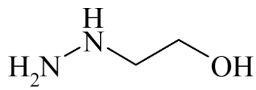
Because UDMH forms a more stable liquid than hydrazine, particularly at lower temperatures, it is often used instead of or in mixtures with hydrazine. UDMH was used in the second stage of the Vanguard [6]. The liquid propellant Aerozine-50 (A-50) contains by specification approximately 51 wt% hydrazine and at least 47 wt% UDMH. Thus, A-50 is a blend of a volatile fuel (UDMH) and an endothermic one (N_2H_4), which combines the handling hazards of low flash point and wide flammable range. It was used to power the Titan II launch vehicle for the *Gemini* spacecraft as well as the second stage of *Delta II*.

The Occupational Safety and Health Administration (OSHA) established limits or thresholds on the allowable exposure and concentration for most propellant chemicals. The OSHA 8-hr personnel exposure limit for vapor of UDMH is 0.5 ppm [7]. The carcinogenicity of UDMH has been investigated by several international organizations [8,9]. These studies have confirmed that there is an increase in incidence of cancers after exposure to UDMH.

In contrast to UDMH, there is a good intermolecular attraction in HEH due to strong hydrogen bonding. Table 1 provides a comparison of some physical properties of UDMH and HEH. As indicated in Table 1, vapor pressure of HEH at room temperature is much lower than UDMH. In addition, hazardous properties of HEH are only limited to oral consumption and skin contact [10].

It is desirable to have liquid propellants with low freezing points for their use in low-temperature conditions. As seen in

Table 1
Comparison of physical properties of UDMH and HEH

Property	UDMH [6]	HEH [18, 19]
Molecular formula	$C_2H_8N_2$	$C_2H_8N_2O$
Molecular weight	60.10	76.10
Molecular structure		
Liquid density, 25°C (g/mL)	0.786	1.123
Boiling point (°C)	62.3	155–160 (at 32 mmHg) 148–152 (at 30 mmHg) 127 (at 17 mmHg)
Freezing point (°C)	−57.2	−70
Flash point (°C)	−15	74
Refractive index (n_{25}^{D})	1.4053	1.4885
Liquid viscosity, 25°C [mPa.s (= cP)]	0.492	147
Vapor pressure (mmHg)	167.25 at 25°C	<1 at 25°C 4 at 110°C
Heat of vaporization at boiling point (kJ/mol)	32.623	76.384[a]

[a]Value was obtained from the Clausius-Clapeyron equation [13].

Table 1, HEH has a low freezing point, which permits operation of rockets in cold weather. It has relatively high density compared to UDMH so that it may be introduced as an appropriate liquid propellant.

The use of pure HEH as liquid propellant can cause some troubles for motor engines, such as:

1. For high-viscosity propellants, both pumping and engine–system calibration become difficult. Propellants with high vapor pressure, such as liquid oxygen, liquid hydrogen,

and other liquefied gases, require special design provisions, unusual handling techniques, and special low-temperature materials. As indicated in Table 1, HEH has relatively high viscosity (about 300 times that of UDMH) and very low vapor pressure. For HEH, the high viscosity may increase the risk of difficult system calibration, but the low vapor pressure decreases the risk of volatilization and inhalation exposure.

2. The high boiling point of HEH may also impact its vaporization and resulting propellant performance.

Results and Discussion

Two important considerations in the design of liquid chemical rocket engines are the propellant feeding and the ignition system, both of which can be optimized using binary mixtures of UDMH/HEH. It will be shown that shortcomings of pure UDMH and HEH can be minimized by suitable combinations of these. Because both UDMH and HEH are hydrazine derivatives, there are favorable intermolecular attractions in binary mixtures of UDMH/HEH.

Synthesis of HEH and Preparation of Binary Mixtures of UDMH/HEH

In order to study desirable physical properties of binary mixtures of UDMH/HEH, UDMH was purchased from Merck Company (KGaA, Darmstadt, Germany). Laboratory synthesis of HEH has been made with a purity of 98% by the reported procedure in which hydrazine hydrate has reacted with gaseous ethylene oxide [11]. The excess hydrazine hydrate and water are removed by distillation under reduced pressure of 25 to 30 mmHg at temperature range 50 to 55°C. Then, HEH is recovered from the residue by distillation at 112 to 115°C under reduced pressure of 5 to 6 mmHg.

Because UDMH is the major component of binary mixtures of UDMH/HEH, nine different weight percentages of HEH (5.226, 9.875, 14.26, 19.05, 24.79, 31.08, 36.40, 39.94, and 45.14%) were used to compare the effect of the addition of HEH to UDMH.

It should be mentioned that each physical property was measured three times and the average value is reported.

Density

A dense liquid propellant is suitable to accommodate a large mass of propellants in a given vehicle tank space that can permit a small vehicle construction. Thus, this situation provides a relatively low structural vehicle mass and low aerodynamic drag. Moreover, it has an important effect on the maximum flight velocity and range of any rocket-powered vehicle or missile flying within the Earth's atmosphere.

To determine the density of binary mixture of UDMH/HEH experimentally, the standard ASTM D 1217 method [12] was used. Figure 1 shows the measured density of mixtures at 293 K versus mass percentage of HEH. As can be seen, there is a linear relationship, with a relatively high slope, between the measured density of mixtures and mass percentage of HEH. However, if pumping and engine–system calibration can allow, it is suitable to have high percentages of HEH in mixtures.

To estimate the density of binary mixture of UDMH/HEH, we can use Eq. (1) to calculate density of mixture, ρ_{mix}, from the measured density value of pure UDMH and HEH:

$$\rho_{mix} = \frac{100}{\sum_{i=1}^{n} \frac{m_i}{\rho_i}} \tag{1}$$

where m_i and ρ_i are the weight percentage and density of component i in the mixture, respectively. The calculated and measured densities of mixtures at 293 K are also compared in Fig. 1.

The best fit of the measured and calculated values can be given as follows:

$$\rho_{meas} = 2.97 \times 10^{-3}\ c_H + 0.79 \tag{2}$$

$$\rho_{calc} = 2.60 \times 10^{-3}\ c_H + 0.78 \tag{3}$$

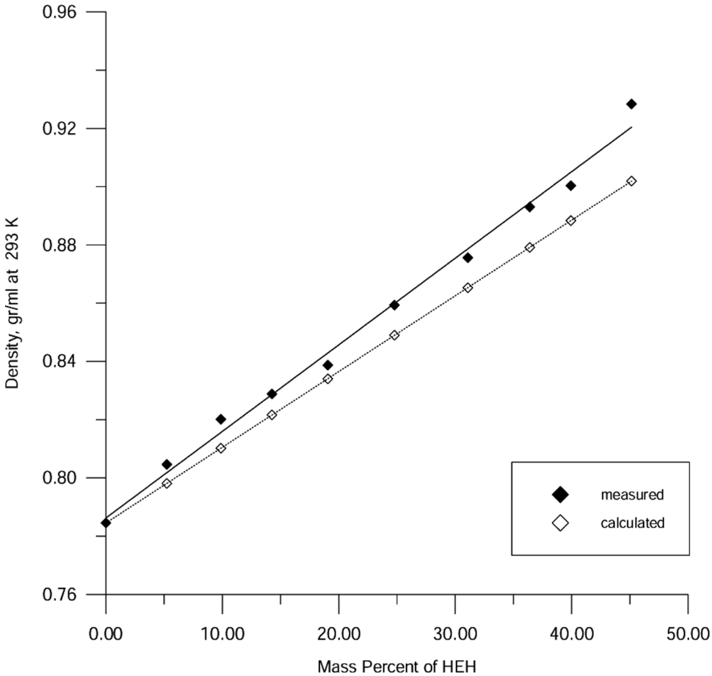


Figure 1. Measured and calculated density of binary mixture of UDMH/HEH versus mass percentage of HEH.

where c_H is defined in terms of masses of HEH (m_{HEH}) and UDMH (m_{UDMH}) as:

$$c_H = \frac{m_{HEH}}{m_{HEH} + m_{UDMH}} \times 100 \tag{4}$$

However, the calculated and measured values are in reasonable agreement.

Boiling Point

A high boiling or decomposition temperature is desirable for propellants that are used for thrust chamber cooling. According to Table 1, the high boiling point and extremely low vapor pressure of HEH confirm the very low volatility of this compound.

Increasing the boiling point of binary mixtures of UDMH/HEH may arise from colligative properties.

Boiling points of binary mixtures of UDMH/HEH have been measured at 790 mbar (0.78 atm) using a BUCHI-545 (BUCHI Labortechnic AG, Switzerland). The measured and calculated values [13] at standard pressure of 1 atm are shown in Fig. 2. It should be mentioned that the Clausius-Clapeyron equation has been used to estimate the corresponding boiling point of HEH at 1 atm. Equations (5) and (6) show equations of the best fits of data given in Fig. 2 for both measured and calculated results:

$$T_{b,meas} = 3.500 \times 10^{-3} c_H^2 + 190.9 \times 10^{-3} c_H + 335.9 \quad (5)$$

$$T_{b,calc} = 245.9 \times 10^{-3} c_H + 335.4 \quad (6)$$

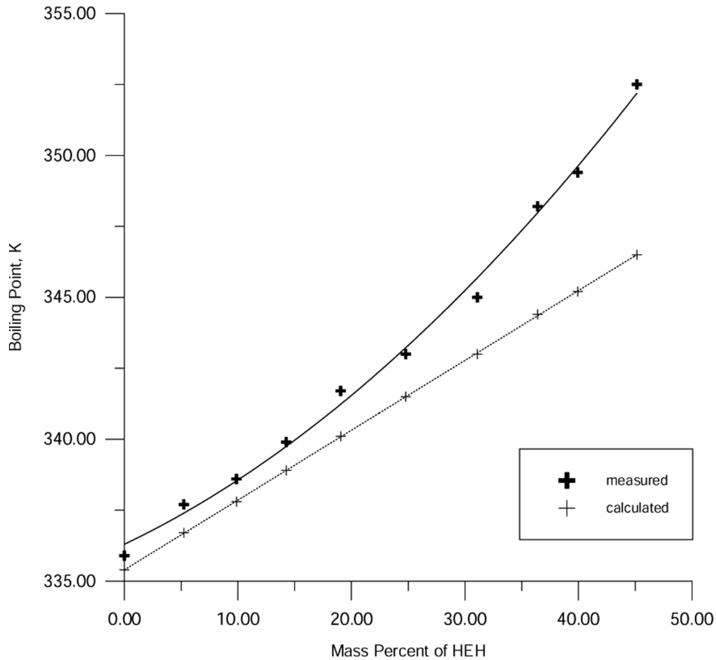
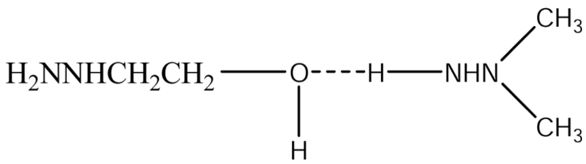


Figure 2. Measured and calculated boiling point of binary mixture of UDMH/HEH versus mass percentage of HEH.

The hydrogen bonding is formed between hydroxyl group of HEH and amino group of neighbor UDMH as:



As indicated in Fig. 2, due to the formation of hydrogen bonding between HEH and UDMH, binary mixtures of UDMH/HEH show larger deviations from ideality by increasing the mass percentag of HEH. The measured boiling point of mixture at a specified composition, which is higher than the corresponding calculated value, is attributed to the hydrogen bonding.

Viscosity

Viscosities of binary mixtures of UDMH/HEH were measured in accordance with international standard method (ASTM D 445) [14]. Figure 3 shows that increasing the mass percentage of HEH has no appreciable effect on viscosity up to 40% of HEH. This behavior of binary mixtures of UDMH/HEH is suitable for pumping and engine–system calibration. As seen in Fig. 3, the calculated results using the method of Teja and Rice [15] are also given. The best curve fitting of the measured and calculated data are given in Eqs. (7) and (8) as:

$$\eta_{meas} = 1.30 \times 10^{-3} c_H^2 - 7.90 \times 10^{-3} c_H + 0.59 \tag{7}$$

$$\begin{aligned}\eta_{cal} = {} & 1.00 \times 10^{-4} c_H^2 - 1.30 \times 10^{-3} c_H^2 \\ & + 5.30 \times 10 c_H + 0.48\end{aligned} \tag{8}$$

Deviations of the measured values from predicted results [15] become large by increasing the mass percentage of HEH, which may be attributed to nonideality of the system. Furthermore, it can be interpreted as hydrogen bonding between two adjacent

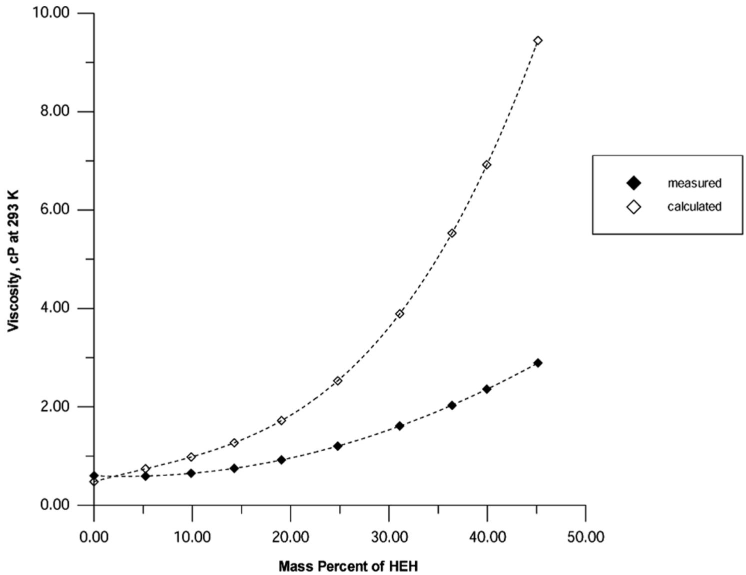


Figure 3. Measured and calculated viscosity of binary mixture of UDMH/HEH versus mass percentage of HEH.

HEH molecules is much larger than pair of UDMH and HEH molecules. For example, the experimental value of viscosity in a mixture with 31% (in mass percent) of HEH is within about 0.33 of predicted value. Viscosity of this combination was increased only 1 cP. Thus, this situation is suitable for a liquid propellant rocket engine that has been designated for UDMH because if the viscosity of the propellant is too high, then pumping and engine–system calibration become difficult.

Vapor Pressure

Appreciable lowering vapor pressures of binary mixtures of UDMH/HEH can be expected by addition of HEH to UDMH because the difference between the vapor pressure of the two components at room temperature is very high. Reducing vapor pressure of UDMH by addition of HEH permits not only easier handling of the propellants but provides a more effective pump design in applications where the propellant is pumped. According to the latest experimental data, the vapor pressure of pure UDMH as a function of temperature can be given as follows [4]:

$$\ln p = 22.394289 - \frac{6551.0134}{T} + \frac{424700.9}{T^2} \tag{9}$$

where p and T are in mmHg and K, respectively. Because precise measurement of vapor pressure of a low volatile solution of binary mixtures UDMH/HEH is difficult at room temperature, vapor pressures of binary mixtures of UDMH/HEH at 25°C were determined indirectly by the Clausius-Clapeyron equation and mixing rule [16]. The interaction parameter of enthalpy of vaporization for a binary mixture of UDMH/HEH can be obtained from the geometric mean of both components [17]; that is, $\Delta H_{V_{ij}} = (\Delta H_{V_I} \Delta H_{V_j})^{\frac{1}{2}}$. Figure 4 shows the changes of vapor pressures for both ideal (Raoult's law) and real solutions at 25°C. Equations (10) and (11) show the best fit of measured and calculated vapor pressure data given in Fig. 4.

$$p_{meas} = -299.9 \times 10^{-2} c_H + 168.5 \tag{10}$$

$$p_{calc} = -143.9 \times 10^{-2} c_H + 167.6 \tag{11}$$

As seen in Fig. 4, the trend of decreasing vapor pressures by using Raoult's law for an ideal solution is much lower than for a real solution. Thus, appreciably lower vapor pressures may arise from the presence of hydrogen bonding that give negative deviations from Raoult's law. For example, the 30/70 HEH/UDMH vapor pressure is about 50% of pure UDMH, thus potentially reducing the risk of exposure by a corresponding amount.

Hypergolicity

UDMH and HEH with NTO and red fuming nitric acid (RFNA) are spontaneously ignitable and so do not require an ignition

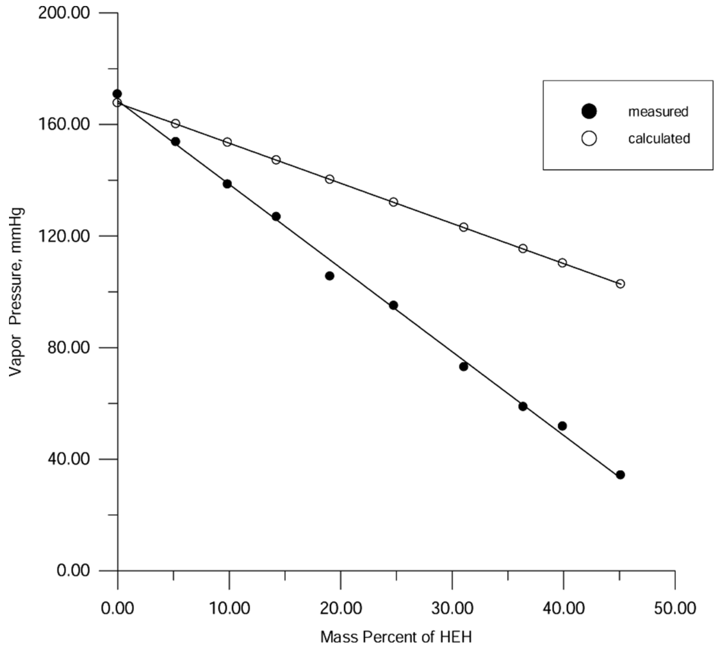


Figure 4. Measured and calculated vapor pressures of binary mixture of UDMH/HEH versus mass percentage of HEH.

system. Because burning is initiated as the oxidizer and the fuel come into contact with each other, they can be called *hypergolic propellants*. Elimination of the ignition system is usually desirable because it simplifies the propulsion system.

Conclusions

Hydrazine derivatives currently as hypergolic propellants such as UDMH have good performance but present an occupational health risk because of the high vapor pressures. One of the primary advantages of the use of binary mixtures of UDMH/HEH is their low vapor pressures with respect to UDMH. Binary mixtures of UDMH/HEH provide an excellent combination of favorable attributes of both UDMH and HEH such as good temperature variation, liquid state, and hypergolicity with NTO and RFNA, and they possess desirable properties including higher boiling points and reduced vapor pressures compared to pure UDMH. Several important results can also be obtained from a study of physical properties of binary mixtures of UDMH/HEH:

1. The ratio of density of pure HEH to UDMH at 25°C is 1.43, which shows a relatively low structural vehicle mass and low aerodynamic drag by increasing the weight percentage of HEH.
2. Experimental determination of the viscosity of UDMH/HEH mixture shows that the viscosity does not change appreciably up to 40% of HEH with respect to theoretically predicted values.
3. Increasing boiling points and lowering vapor pressures of UDMH/HEH solution are related to intermolecular attractions. The existence of hydrogen bonding between UDMH and HEH reduces the volatility of UDMH, which can decrease the vapor pressure of poisonous UDMH. This matter is very important for improved safety of personnel and environmental considerations.
4. In contrast to pure UDMH, the organic compound HEH has relatively high viscosity and boiling point and very low vapor pressure, which can significantly reduce the hazardous properties of UDMH.

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