The Outlook for the Use of Pseudopolymorphic Solvates in Energetic Materials

David B. LEMPERT[*] and Nikita V. CHUKANOV

Institute of Problems of Chemical Physics of Russian Academy of Sciences, Semenov av. 1, Chernogolovka, Moscow region, 142432 Russia
[*]*E-mail: lempert@icp.ac.ru*

Abstract: An analysis of the ballistic characteristics of propellants based on energetic pseudopolymorphic solvates has been performed. It is shown that the ballistic efficiency of solid composite propellants containing γ-HMX or α-CL-20 can be improved considerably by means of the introduction of small molecules into the structural cavities present in the crystal structures of these polymorphs. This effect may appear when small molecules (*e.g.* water, hydrazine, ethanol) enter into the crystal structure of the main component with no changes in the lattice parameters of the latter.

Keywords: γ-HMX hydrate, α-CL-20 hydrate, propellant, ballistic efficiency, density

1 Introduction

In some crystal solvates, the solvent is not an indispensable part of the crystal structure and merely occupies structural cavities in the crystal. This type of solvate has been called a pseudopolymorphic solvate [1, 2]. In such crystals, the sites occupied by the solvent (guest) molecules can be only partially occupied. For example, the γ-modification of HMX and the α-modification of CL-20 are well-known energetic pseudopolymorphic hydrates [3, 4]. In their crystal structures, water molecules are present in fixed, but partially vacant sites. In particular, in the sample of γ-HMX investigated in [3] the molecules of HMX and H_2O are present at the ratio 4:1, and the occupancy factor of H_2O is equal to 0.5. Complete occupation of this site would correspond to a water content

of about 3 wt.%.

The introduction of water molecules into the structural voids of such energetic compounds does not affect practically the lattice parameters and, consequently, results in enhancement of the density. On the other hand, pseudopolymorphic hydrates differ from their anhydrous counterparts in their standard formation enthalpies which decrease strongly because of the presence of water. Both these factors should have an influence upon the ballistic efficiency of propellants containing such compounds. This paper provides estimations of the ballistic characteristics for some solid composite propellants based on γ-HMX and α-CL-20 hydrates.

2   The States of Water in Hydrates of Energetic Nitramines

In γ-HMX (monoclinic, space group *Pn*, *a* = 13.27, *b* = 7.90, *c* = 10.95 Å, β = 106.8°, d_{calc} = 1.82 g/cm^3 [3]) water is situated in the structural voids between the HMX molecules, with the shortest distance between the O atom of the H_2O molecule and an O atom of the -NO_2 group of 2.91 Å, which corresponds to a weak (about 2 kcal/mol) hydrogen bond.
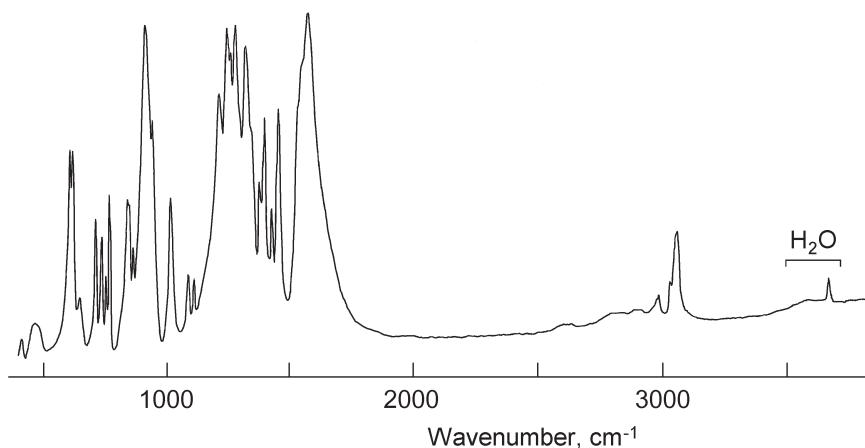
Figure 1.   Infrared spectrum of γ-HMX hydrate.

The infrared (IR) spectra of γ-HMX and α-CL-20 have been published elsewhere [5, 6], with the assignment of most of the absorption bands. However some details concerning hydrogen bonding need to be discussed. In the IR

spectrum of γ-HMX (Figure 1), two bands due to O-H-stretching vibrations are observed. One of them, located at 3672 cm^{-1}, corresponds to a very weak hydrogen bond. The other, with the absorption maximum at 3590 cm^{-1}, is assigned to stretching vibrations of hydroxyl groups forming somewhat stronger hydrogen bonds. The corresponding energies of the hydrogen bonds may be estimated using the correlation [7]: $-\Delta H$ (kJ/mol) $= 28.5\, \Delta v : (\Delta v + 269)$, where Δv (cm^{-1}) $= v_0 - v$ is the wavenumber shift for the band of O-H-stretching vibrations induced by hydrogen bonding. Taking into account that the mean wavenumber for the doublet of O-H-stretching vibrations of free (non-H-bonded) H_2O molecules is $v_0 = 3710$ cm^{-1}, we obtain the following values for hydrogen bond energies of water molecule in γ-HMX: $-\Delta H_1 = 3.53$ kJ/mol, $-\Delta H_2 = 8.79$ kJ/mol.
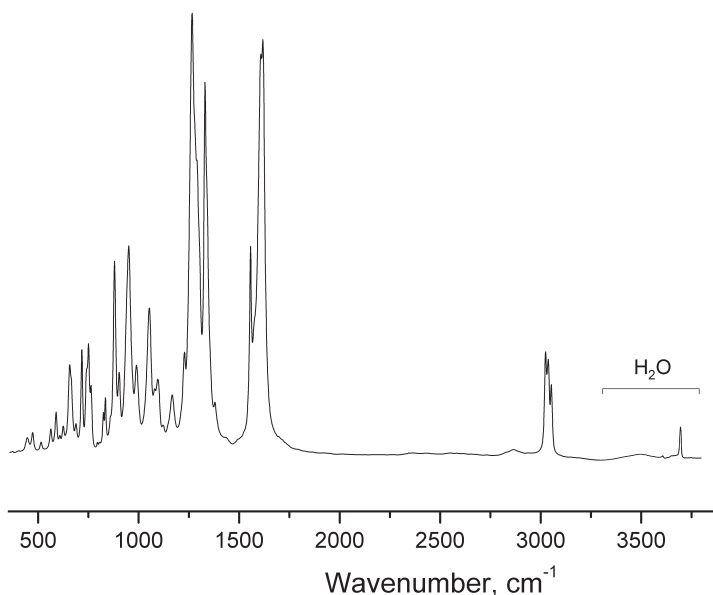
Figure 2.   Infrared spectrum of α-CL-20 hydrate.

In α-CL-20 hydrate (orthorhombic, space group *Pbca*, $a = 9.603(3)$ Å, $b = 13.304(3)$ Å, $c = 23.653(4)$ Å, $V = 3021.79(9)$ Å^3; $d_{calc} = 1.925$ g/cm^3 for anhydrous α-CL-20 $d_{calc} = 1.965(7)$ g/cm^3 for the investigated sample [4]), H_2O molecules occupy three sites inside the elongated structural cavities. Two extreme sites may be occupied simultaneously, corresponding to a water content of about 4 wt.%. However there are steric hindrances for the simultaneous occupation of adjacent (*i.e.* central and extreme) sites.

As one can see from the IR spectrum of α-CL-20 hydrate (Figure 2), one

H atom of the H_2O molecule is almost free, and the other is H-bonded. The corresponding wavenumbers of the O-H-stretching vibrations are ~3700 and ~3500 cm^{-1}, respectively. The latter value corresponds to a hydrogen bond energy of 12.49 kJ/mol. The total dehydration energy of α-CL-20 hydrate, estimated from calorimetric data [8], is 15.5 kJ/mol. The latter value includes contributions from hydrogen and van der Waals interactions of H_2O molecules in α-CL-20 hydrate.

3 Ballistic Efficiency of CL-20 and HMX Hydrates when Used as Oxidizers in Solid Composite Propellants

The energies of interactions of H_2O molecules in the crystals of α-CL-20 and γ-HMX hydrates, estimated from IR spectroscopic data [15.5 kJ/(mol H_2O) = 883 kJ/(kg H_2O) and 12.3 kJ/(mol H_2O) = 683 kJ/(kg H_2O) respectively, see above] can be used for the calculation of their standard formation enthalpies ΔH^0_f for known water contents in the crystals:

$\Delta H^0_f = (1-a)^* \Delta H^0_{f\ \alpha CL-20} + a \cdot (\Delta H^0_{f\ H_2O\ gas} + 861)$ for α-CL-20 hydrates;

$\Delta H^0_f = (1-a)^* \Delta H^0_{f\ \gamma HMX} + a \cdot (\Delta H^0_{f\ H_2O\ gas} + 683)$ for γ-HMX hydrates

where a is the mass fraction of water in the solid hydrate, and $\Delta H^0_{f\ \alpha CL-20}$ and $\Delta H^0_{f\ \gamma HMX}$ are the standard formation enthalpies of the anhydrous oxidizers, $\Delta H^0_{f\ H_2O\ gas}$ = -13442 kJ/kg. The presence of water in the structural cavities of pseudopolymorphic solvates does not affect their lattice parameters. Consequently, the densities of α-CL-20 and γ-HMX hydrates can be calculated using the formula $d = d_0/(1-a)$ where d_0 is the density of the anhydrous oxidizer.

For the calculation of the efficiency of the energetic compounds under consideration as components of solid composite propellants, the following compositions close to practical ones have been considered: 20 wt.% Al + 14 wt.% of active binder ($C_{18.96}H_{34.64}N_{19.16}O_{29.32}$, ΔH^o_f = -757 kJ/kg, d = 1.49 g/cm^3 [9] + 10 wt.% of ammonium perchlorate + 56 wt.% of CL-20 or HMX. The calculation of the specific impulse Isp and the combustion temperature Tc were performed using the standard code "TERRA" for the calculation of thermochemical equilibria [10], at pressures in the combustion chamber and at the nozzle exit section of 4.0 and 0.1 MPa, respectively. As a result, for the composition with anhydrous α-CL-20, it was found that the specific impulse is equal to 256.4 s, the temperature in the combustion chamber is Tc = 3973 K and the density ρ of the formulation is equal to 1.960 g/cm^3 (Table 1).

Table 1. Energetic parameters of the formulations 20 wt.% Al + 14 wt.% of active binder + 10 wt.% of ammonium chlorate(VII) + 56 wt.% of the oxidizer under consideration

| | Oxidizer: the modification of CL-20 and the kind of the adduct | | | | | |
	ε-CL-20	α-CL-20 anhydrous	α-CL-20 with 2 wt.% of water	α-CL-20 with 4 wt.% of water	α-CL-20 with 3.5 wt.% of hydrazine	α-CL-20 with 5 wt.% of ethanol
Formulation number	1	2	3	4	5	6
Isp, s	257.3	256.4	256.2	255.8	258.0	256.6
ρ, g/cm^3	2.025	1.960	1.982	2.004	2.000	2.017
Tc, K	3985	3973	3953	3931	3910	3816
$I(1)$, s	269.8	262.4	264.4	266.2	267.9	268.3
$I(2)$, s	268.6	264.5	265.3	266.0	268.0	267.4
$I(3)$, s	265.5	263.0	263.2	263.4	265.5	264.5
$dI(1)$, s	7.4	0.0	2.0	3.8	5.5	5.9
$dI(2)$, s	4.2	0.0	0.8	1.5	3.5	3.0
$dI(3)$, s	2.5	0.0	0.2	0.4	2.5	1.6

The replacement of anhydrous α-CL-20 by its hydrate containing 4 wt.% H_2O resulted in $Isp = 255.8$ s, $Tc = 3931$ K, $\rho = 2.004$ g/cm^3, *i.e. Isp* was reduced by 1.2 s, but the composition density was increased by ~0.045 g/cm^3. For the hydrate with 2 wt.% H_2O, $Isp = 256.2$ s, $Tc = 3954$ K, $\rho = 1.982$ g/cm^3, *i.e. Isp* was reduced by 0.2 s, but the composition density was increased by ~0.022 g/cm^3. It is well known that the influence of the propellant density may vary, depending on the rocket stage, and the weight and mass characteristics of the rocket engine. For this reason, the ballistic efficiency of solid composite propellants has been estimated in two different ways:

A) For three-stage rockets – by the empirical formulae [11] for the estimation of so-called effective impulses *Ief(n)* on the first, the second and the third stages:

$Ief(1) = Isp + 100 \cdot (\rho - 1.9)$

$Ief(2) = Isp + 50 \cdot (\rho - 1.8)$

$Ief(3) = Isp + 25 \cdot (\rho - 1.7)$

B) For single-stage rockets – by the modified Tsiolkovsky formula [12]:

$W = g_0 \cdot Isp \cdot \ln(1 + F \cdot \rho)$,

where W (m/s) is the velocity increase of the rocket through all of the propellant being burned-out, $F = V_p/M_e$ (cm^3/g) is the ratio of the propellant volume V_p to

the empty weight M_e of the rocket, $g_0 = 9.806$ m/s².

From the above formulae, it follows that for the formulation with individual α-CL-20 the values of *Ief(1), Ief(2)* and *Ief(3)* are equal to 262.4, 264.5 and 263.0, respectively. For the formulation with α-CL-20 hydrate containing 4 wt.% H_2O, the corresponding values are higher, with the largest increase of the effective impulse due to the use of the hydrated oxidizer being on the first stage (dI(1) = 3.8 s). The increase of *Ief(n)* on the second and the third stages is substantially lower: dI(2) = 1.5 s, dI(3) = 0.4 s. Consequently, the replacement of α-CL-20 by its hydrate results in a considerable enhancement of ballistic efficiency on the first stage, with a minor advantage on the second stage. In the formulation with α-CL-20 containing 2 wt.% H_2O, the increase in effective impulse on all stages is approximately half of the above values.

It should be noted that even rather strong interactions of α-CL-20 with incorporated water molecules (*e.g.* hydrogen bonding with energies up to 30 kJ per mole of H_2O, or up to ~1500 kJ/kg) results in only minor changes in *Isp* and *Ief(n)* [dI ≈ dI(n) ≈ 0.027 s per 100 kJ/(kg H_2O)].

The replacement of anhydrous γ-HMX by its hydrated analogue also results in an enhancement of *Ief(n)*, but in this case the advantage in ballistic efficiency is less compared with the α-CL-20 hydrate (Table 2).

Table 2.   Energetic parameters of the formulations 20 wt.% Al + 14 wt.% of active binder + 10 wt.% of ammonium chlorate(VII) + 56 wt.% of the oxidizer under consideration

Oxidizer	γ-HMX anhydrous	γ-HMX with 2 wt.% H_2O	γ-HMX with 3 wt.% H_2O
Isp, s	259.9	259.5	259.2
ρ, g/cm³	1.898	1.919	1.929
Tc, K	3777	3764	3762
I(1), s	259.6	261.3	262.1
I(2), s	264.8	265.4	265.7
I(3), s	264.8	264.9	264.9
dI(1), s	0.0	1.7	2.5
dI(2), s	0.0	0.6	0.9
dI(3), s	0.0	0.1	0.1

The above consideration shows that even the introduction of an energy-unfavorable substance like water in the oxidizer crystal structure may result in improvements in the ballistic characteristics of the propellant, at least on the lower stages. The introduction of molecules of combustible compounds (*e.g.* hydrazine,

ammonia or small organic molecules) into the structural voids of energetic substances would result in a more significant enhancement of ballistic efficiency.

The structural cavity in α-CL-20, having a length of about 5 Å, is large enough to contain a hydrazine molecule (one molecule per two molecules of CL-20, *i.e.* 3.7 wt.%) and possibly an ethanol molecule (also one molecule per two molecules of CL-20, *i.e.* 5.3 wt.%), and some other linear molecules containing two or three atoms of C, N and/or O, excepting hydrogen.

As was shown above, the change of standard formation enthalpy by 40-60 kJ per mole of guest compound (at a content of the latter of about 3-4 wt.%) does not have an important influence on the specific impulse of the composition containing ~50 wt.% CL-20. However our calculations demonstrate that the introduction of hydrazine or ethanol into the structural cavities of α-CL-20 would result in a substantial increase of *Ief* (see Table 1, compositions Nos. 5 and 6). Basically, this is a result of the increase in density. In addition, the introduction of organic compounds or hydrazine in the composition results in an increase in *Ief*, unlike the case with water as the guest molecule. In general, compositions Nos. 5 and 6 show substantially improved characteristics, as compared with the analogous compositions with water.

The values of *Isp* for some compositions based on solid solvates of α-CL-20 (Table 1) approach that of the analogous compositions based on the high-density ε-CL-20 modification. However, the latter shows somewhat better ballistic efficiency.

Table 3.   The increase of W (%) in comparison with Formulation 2 from Table 1

Formulation number from Table 1	$F = 0.5$ L/kg	$F = 3$ L/kg	$F = 9$ L/kg
1	2.7	1.8	1.4
4	1.4	0.8	0.5
5	2.1	1.5	1.3
6	2.2	1.3	1.0

As was noted above, a comparison of the relative ballistic efficiency of the formulations under consideration has also been carried out with regard to single-stage rockets with different F ratios of the propellant volume V_p to the empty weight M_e of the rocket, *i.e.* for rockets with different functions. The results given in Table 3 demonstrate that for rockets with a relatively low F value of 0.5, the enhancement of the characteristic velocity W due to the replacement of anhydrous α-CL-20 by its pseudopolymorphic solvates with different guest molecules would be ~1.5% for hydrazine and ~2% for ethanol. This advantage,

achieved due to the increase in the density, diminishes with increase in F. In particular, for $F = 9$ L/kg, the increase in the characteristic velocity due to the introduction of 4 wt.% H_2O into α-CL-20 is only ~0.5%. The increase in the characteristic velocity due to the introduction of 3 wt.% H_2O into α-CL-20 at $F = 0.5$, 3 and 9 L/kg is equal to 0.9, 0.3 and 0.2%, respectively.

The use of hypothetical solid solvates of α-CL-20 with 5 wt.% ethanol or with 3.5 wt.% hydrazine, would result in significant enhancement of the characteristic velocity (at least by 1%, even for rockets with high F values) because of the increase in both density and specific impulse. Actually, one cannot predict all of the properties of such hypothetical solid solvates. Even if they exist they may be not stable enough, especially solvates with hydrazine: the interaction of hydrazine with NO_2-groups would be rather strong, the more so because these units would be neighbours in the same molecule. On the other hand, a solid matrix can play an inhibitory role and prevent the best orientation of the guest molecule to be favourable for its reaction with the host.

In the above examples, α-CL-20 and γ-HMX have been considered as model compounds: at present, only high-density polymorphs ε-CL-20 and β-HMX are of practical use. However the introduction of small molecules into the structural voids of energetic compounds having only low-density modifications, would provide significant enhancement of the ballistic efficiency because of the increase in density. Certainly, this way of enhancing a propellant's ballistic efficiency can be only possible if the pseudopolymorphic solvates used possess acceptable thermal stability . The stability of pseudopolymorphic hydrates can differ. Our observations show that no detectable changes in the content of the structural water occur on storage of α-CL-20 hydrate at room temperature during several years: the initial stage of dehydration can be detected only at temperatures above 110 °C [13, 14]. On the other hand, partial dehydration (by several 10%) of γ-HMX occurs at room temperature during two years.

It is probable that the impact sensitivity of the hydrates under consideration would be considerably lower than the sensitivity of the anhydrous compounds, because the presence of water (even in a portion as small as 4%) reduces drastically the maximal heat Q_{max} and the temperature T_{expl} of the explosion. It is known that there is a nearly linear inverse correlation between these parameters and sensitivity [15, 16]. Actually, the calculated T_{expl} for anhydrous α-CL-20 at 3000 MPa is equal to 4203 K, while in case of the hydrate with 2 and 4 wt.% water, it is reduced to 4110 and 4000 K, respectively. This gives support to the hope that hydrates of energetic compounds would have lower impact sensitivities than those of their anhydrous analogues.

4   Conclusions

Some molecular crystals composed of relatively large molecules (including the γ-modification of HMX and the α-modification of CL-20) can hold water molecules in the structural cavities of the crystals with no change in the crystal lattice parameters. As a result, solid composite propellants containing such solid hydrates may exhibit increased density and increased ballistic efficiency as compared with propellants based on their anhydrous counterparts (despite the specific impulse being decreased).

The size of the cavities in the crystal structure of α-CL-20 makes it possible to place not only water molecules, but also other, larger ones (*e.g.* hydrazine) inside the host. This may result in a higher increase in the propellant ballistic efficiency because of a smaller decrease in the specific impulse, as compared with the solid hydrates.

5   References

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