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Modifying the Wettability of Nitramine Explosives using Anionic, Cationic and Nonionic Surfactants

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Abstract: Wetting behavior of energetic materials surface including cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX) and hexanitrohexaazaisowurtzitane (CL-20) using nonionic (Triton-X), anionic (SDS), and cationic (TTAB) surfactants has been studied by contact angle tensiometry. Results show that TTAB more significantly reduces the contact angle and improves wettability as compared to SDS and Triton-X. The liquid-vapor surface tension γ_{lv} was measured as a function of TTAB surfactant concentration in aqueous solutions and used to construct a Zisman plot to determine the critical surface tension of RDX, HMX and CL-20. The results show that HMX displays the highest degree of wettability while RDX is most difficult to wet. The computed values of the work of spreading complement the previously discussed results where contact angle decreases with increasing surfactant concentration. They also indicate that RDX appears most impacted by the addition of TTAB surfactant. However, the addition of TTAB also has a significant impact on improving the wettability of HMX and CL-20. This wettability study plays an important role in the formation of well-wetted energetic surfaces needed for efficient wet milling, coating and granulation processes.

Keywords: Wettabilitty · Nitramines · surfactant · RDX · HMX · CL-20

1 Introduction

Wettability plays an important role in numerous technological applications, such as: oil recovery, coating, adhesion, flotation, printing, detergency and the cosmetics industry [1–7]. Wettability is also considered one of the primary factors leads to higher mechanical stability of energetic materials due to improved wetting of the liquid (polymeric binder) on a particulate explosive [8]. The friction sensitivity of primary explosives is also affected by the wettability [9]. Wettability studies usually involve the measurement of contact angles (θ) as the primary data, which indicate the degree of wetting when a solid and liquid interact. Small contact angles correspond to high wettability, while large contact angles correspond to low wettability (Figure 1). The contact angle is affected by the chemical composition, roughness, the surface charge of the solid, and by the liquid properties [10–12]. The sessile drop method is a technique that directly measures contact angle on a solid sample and is used to measure the contact angle between the liquid and the compressed explosive powder in this work. The method is usually used for smooth, homogeneous, impermeable and non-deformable surfaces. Due to the inherent porous architecture of compressed powder cakes, liquid penetration may occur depending on the wettability of the individual particles. This type of liquid penetration would eliminate the potential to utilize the direct measurement method, high surface energy materials resist such liquid penetration. An indirect method to measure the contact angle such as the capillary penetration method [8] could be used as an alternative. For our energetic materials the surface energy is high enough that reproducible wetting was made possible by using identical pellet compression conditions resulting in a low porosity sample.

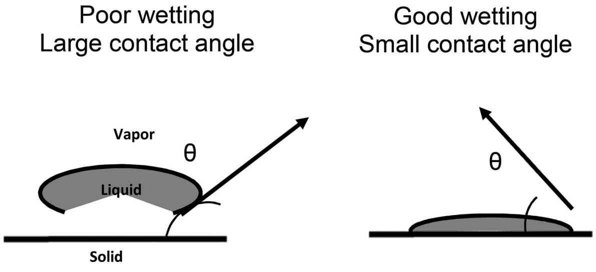

Figure 1. Illustration of contact angle for poor and good wetting.

As first described by Thomas Young [13] in 1805, the contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions (Figure 2):

$$\gamma_{lv}\cos(\theta) = \gamma_{sv} - \gamma_{sl} \quad (1)$$

where γ_{lv}, γ_{sv}, and γ_{sl} represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and θ

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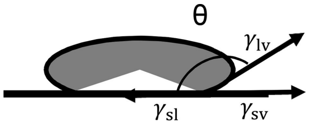


Figure 2. Illustration of surface tension.

is the contact angle. Eq. 1 is referred to as Young's equation, and θ is Young's contact angle.

While the liquid-vapor surface tensions γ_{lv} and the contact angles can be measured directly. Young's equation is then used to determine the solid-liquid surface tension γ_{sl}.

The presence of surfactants in the liquid is an important feature that controls the wetting behavior of a liquid over a substrate. The surfactant has the advantage that it can reduce the liquid-vapor γ_{Lv} and solid-liquid γ_{sl} interfacial tension and promote wetting according to Eq. 1. Influence of surfactants on the contact angle has been studied on numerous materials such as glass [14] mica [15], quartz [16] as well as hydrophobic surfaces such as polytetrafluoroethylene (PTFE) [17] in the presence of either pure or mixture of surfactants.

Previous studies on the wettability of energetic materials (water without surfactant) include values of 78° [18] and 84.1° [19] for RDX using a coated glass slide method. Wettability of single crystalline surfaces of HMX with water result in contact angles of 70°, 60° and 50° for 011, 010 and 110 surfaces, respectively [20].

In this work, the wetting behavior on nitramines of aqueous solutions of the cationic surfactant trimethyl tetradecyl ammonium bromide (TTAB), the anionic surfactant sodium dodecyl sulphate (SDS) and the nonionic surfactant (Triton-X 100) is determined on the basis of contact angle and surface tension measurements.

2 Materials and Methods

2.1 Materials

The surfactants used in this work are sodium dodecyl sulfate (SDS purchased from Sigma-Aldrich), tetradecyltrimethylammonium bromide (TTAB purchased from Fluka) and octylphenol ethoxylate (Triton-X purchased from Chemistry Store). The chemical structures of these surfactants are illustrated in Figure 3. All surfactants were used as received without any further purification. Solutions with different concentrations were prepared containing a single surfactant in deionized water and used later for the surface tension and the contact angle measurements.

0.5 grams of RDX (Class 5, BAE systems, Holston TN) was pressed under 15000 psi using a Carver automatic press (Series NE) to produce several pellets with smooth surfaces. The pressed pellets were used as the substrate for the contact angle measurements. An identical procedure was followed to produce HMX and CL-20 pellets needed for the contact angle measurements. The chemical structure of the three energetic materials are shown in Figure 4.

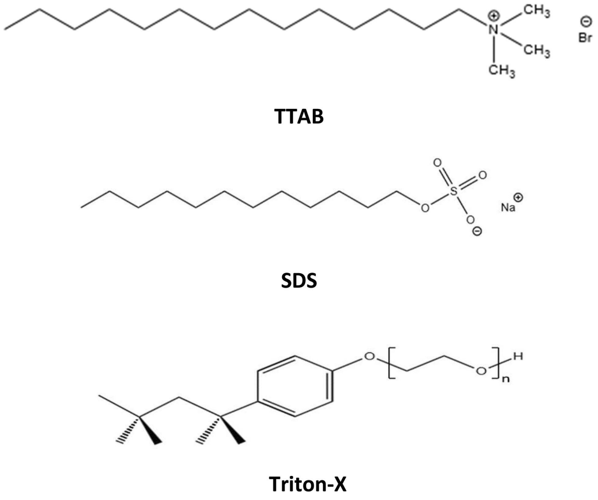


Figure 3. Surfactants chemical structures.

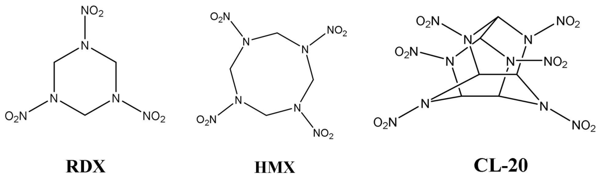


Figure 4. Energetic materials chemical structures.

2.2 Contact Angle Measurements

The measurements of contact angles for the aqueous solutions of surfactants on RDX, HMX and CL-20 were carried out via the sessile drop method with a SCA20 (Dataphysics instruments GmbH, Stuttgart, Germany). The size of the surfactant droplets for all the contact angle measurement was 6 μL. The contact angle measurements on both sides of the drop of a given solution were carried out within 10 seconds after deposition. The measurements were at three different positions on the surface for each surfactant concentration and each pressed explosive surface. The results are mean values of the three measurements, and the standard deviation of the contact angle values was $<2°$.

2.3 Surface Tension Measurements

Surface tension γ_{lv} was measured as a function of surfactant concentration in aqueous solutions for TTAB. The measurements were conducted using the Du Nouy-Padday method [21] with a 3.18 mm diameter aluminum rod hung from a bottom hanging analytical balance (Ohaus Pioneer). This probe is partially submerged vertically into a fluid sample. Then, the fluid is slowly lowered away from the probe and a maximal force is recorded immediately prior to fluid detachment from the probe. This force (F_{max}) correlates linearly to the surface tension of the fluid. The probe was calibrated by determining F_{max} for a series of fluids with known surface tension (water, ethanol, DMSO and dodecane) and using linear regression to develop a calibration curve. Surface tension of the experimental samples was determined from the calibration curve and a measured F_{max} for each experimental solution.

3 Results and Discussion

3.1 Effect of Surfactant Concentration on the Contact Angle

3.1.1 RDX

The resulting contact angles with cationic, anionic and nonionic surfactants is shown as a function of the surfactant concentration normalized by the critical micelle concentration (CMC) of each surfactant on RDX surface in Figure 5. The CMC of each surfactant is shown in Table 1.

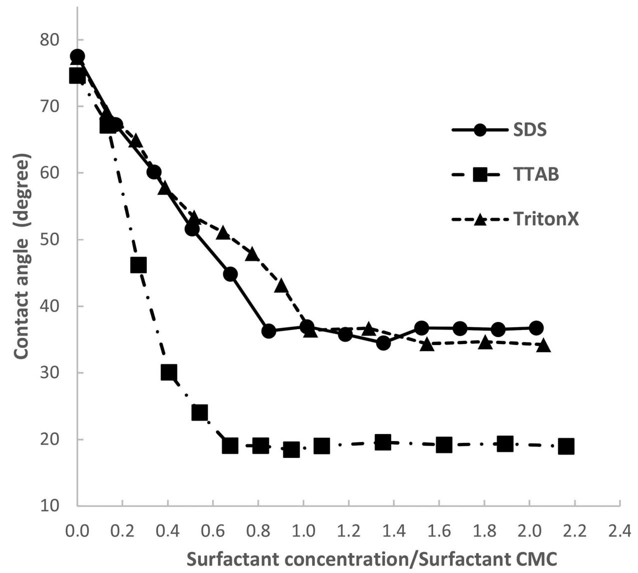


Figure 5. RDX contact angle measurements.

Table 1. CMC surfactant values [22].

Surfactant	Critical Micelle Concentration (mM/L)
TTAB	4.4
SDS	8.2
Triton-X	0.24

The measured contact angle of pure water on the RDX pellet surface is ≅80°. In the presence of the cationic surfactant (TTAB), the contact angle decreases to 20° and attains a plateau value at 70% of CMC. The anionic and nonionic surfactants SDS and Triton-X showed similar behavior and they decreased the contact angle to 36°. The lowest contact angle with SDS was reached at 80% of CMC but with Triton-X was reached at exactly at the CMC value. The decrease of contact angle in the presence of surfactants is due to the adsorption of surfactant molecules on the RDX surface. The final contact angle depends mainly on the orientation of the adsorbed surfactant molecules on the surface. RDX shows a negative charge in aqueous media due to ionization of nitro groups on the surface [23]. Therefore TTAB molecules adsorb on the surface through the positively charged head group by strong electrostatic attraction at a lower concentration in comparison to SDS and Triton-X (Figure 6a). However SDS and Triton-X are adsorbed on the surface via the tail group through hydrogen bonding (Figure 6b and 6c). This implies that TTAB significantly decreases the contact angle and improves wettability compared to SDS and Triton-X.

3.1.2 HMX

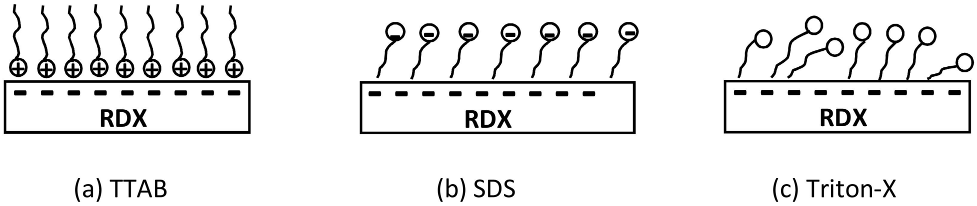
The contact angle of cationic (TTAB), anionic (SDS) and nonionic (Triton-X) surfactant solutions on HMX surface were measured as a function of surfactant concentration. These results are shown in Figure 7 with the surfactant concentration normalized by the surfactant CMC.

The contact angles of HMX in the presence of pure water is ≅62° which is an indication of better wettability than RDX. The lowest contact angle was reached by TTAB at 80% of CMC with a value of 18°. SDS and Triton-X show a similar trend with a slightly higher contact angle of 23° for SDS. HMX also shows a negative surface charge as RDX does in aqueous media due to ionization of nitro groups on the surface. The mechanisms responsible for the adsorption of the three surfactants are similar to RDX due to similarity of the molecular structure of RDX and HMX. The addition of TTAB decreases the contact angle and improves HMX wettability better than SDS and Triton-X.

3.1.1 CL-20

The measured values of contact angle of aqueous solutions of TTAB, SDS and Triton-X surfactants on the CL-20 surface are shown in Figure 8.

The contact angles of CL-20 surface in the presence of pure water is around 70°. The behavior of three surfactants is quite different than RDX and HMX. SDS and TTAB showed similar trends with a minimum contact angle of 30° at 68% of CMC. Triton-X showed a higher contact angle around 40° at the same CMC as SDS and TTAB. However TTAB is still the



(a) TTAB (b) SDS (c) Triton-X

Figure 6. Schematic diagram of adsorption pattern of ionic and nonionic surfactants.

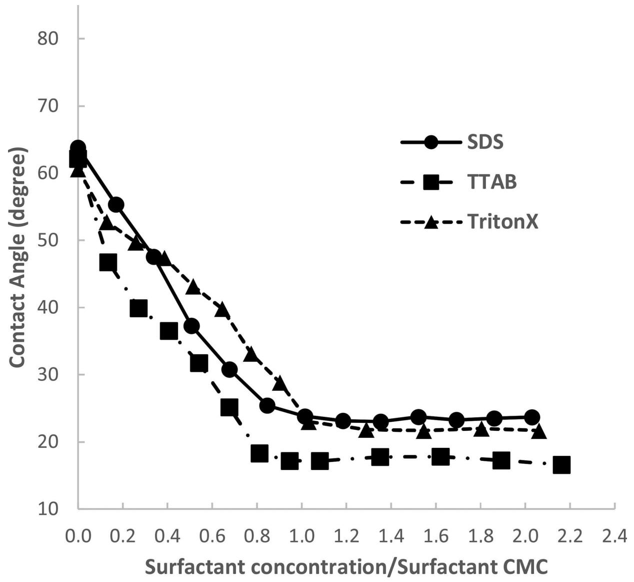


Figure 7. HMX contact angle measurements.

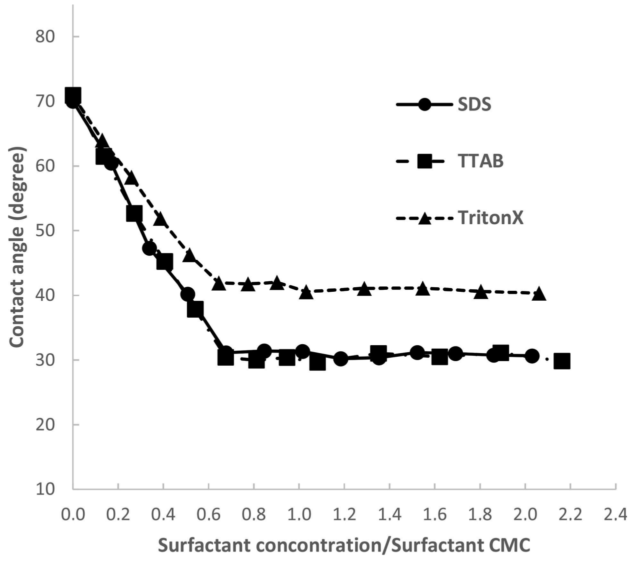


Figure 8. CL-20 contact angle measurements.

best candidate to enhance the contact angle as RDX and HMX with a concentration of 65–80 % of CMC.

3.2 Effect of Surfactant on the Surface Tension

To compute the work of spreading, surface tension γ_{lv} was measured as a function of surfactant concentration in aqueous solutions for TTAB. The results are presented in Figure 9. Surface tension decreases with the addition of surfactant as the surfactant primarily congregates at the vapor-liquid interface breaking up the cohesive forces between water molecules. At some point, for any given surfactant, the hydrophobic tails of the molecules combine to form micelles. After this point, any additional surfactant has minimal impact on fluid surface tension as this additional surfactant goes toward forming more micelles.

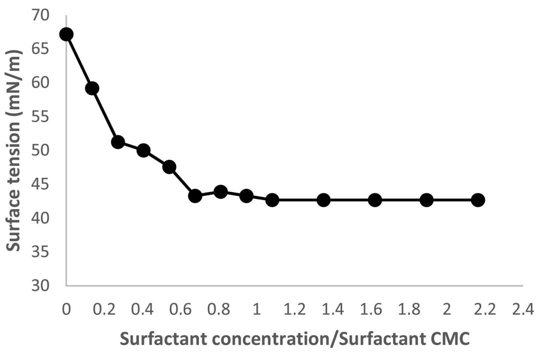


Figure 9. TTAB surface tension measurements.

3.3 Effect of Surfactant Concentration on the Work of Spreading

Zisman plots of cos(θ) vs the liquid-vapor surface tension γ_{lv} are typically used for analysis of both solid material properties and the influence of surfactant [17,24]. Figure 10 shows a Zisman plot of TTAB solutions of varying concentration on RDX, CL-20 and HMX surfaces by replotting the data from Figures 5, 7, 8 and 9.

From the Zisman plot (Figure 10), the critical surface tension of the solid materials can be calculated by linearizing the experimental data points and calculating the x-axis value where $\cos(\theta)=1$. Critical surface tension of the three surfaces is in Table 2.

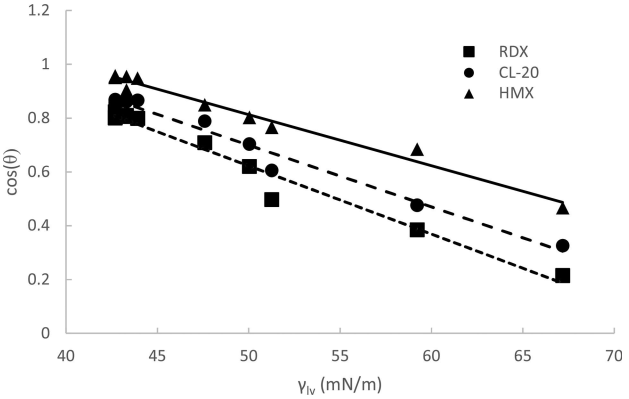


Figure 10. Zisman plot of cos(θ) vs liquid-vapor surface tension for TTAB solutions on RDX CL-20 and HMX.

Table 2. Critical surface tension values computed from Zisman plot.

Energetic Materials	Critical Surface Tension (mN/m)
RDX	35.1
CL-20	36.9
HMX	40.1

Critical surface tension defines the point at which a fluid with the same surface tension or lower will display complete wetting of the solid, meaning that HMX is most wettable, followed by CL-20 and then RDX. The work of spreading (W_s) can be calculated using Eq. 2.

$$W_s = \gamma_{lv}(1 - \cos(\theta)) \tag{2}$$

Work of spreading quantifies how difficult it is for a liquid to spread over a surface. It is dependent on both the applied liquid and the surface energy of the solid material. Generally, a lower W_s signifies easier wetting of the solid surface. The work of spreading is plotted as a function of normalized surfactant concentration in Figure 11.

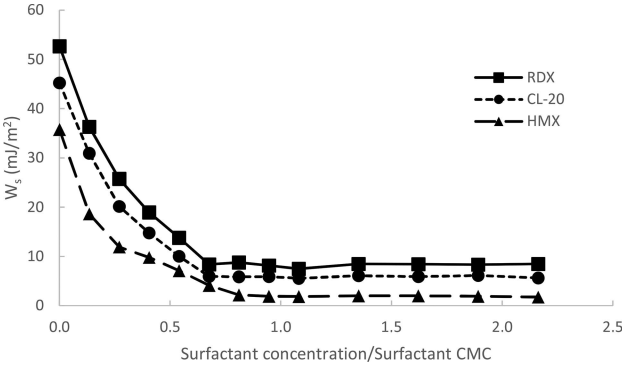


Figure 11. Work of spreading as a function of normalized surfactant concentration for TTAB solutions on RDX, CL-20 and HMX surfaces.

It is apparent in Figure 11 that increased surfactant concentration results in easier wetting. This is confirmed in the previously discussed results where contact angle decreases with increasing surfactant concentration. It is again apparent that HMX is the easiest material to wet and RDX is the most difficult. RDX has the lowest energy surface of the three.

Another interpretation of these data is to subtract the work of spreading at a given surfactant concentration from the work of spreading with no surfactant (Eq. 3). This quantifies the impact of adding surfactant to the liquid. This is plotted for the different surfaces in Figure 12.

$$W_{s0} - W_s \text{ where } W_{s0} = W_s(\mathit{Surfactant\ Conc} = 0) \tag{3}$$

The largest change in the work of spreading upon addition of surfactant occurs on the RDX surface while the smallest change occurs for HMX. In applications where wetting of these energetic surfaces is important, TTAB surfactant will be effective. RDX is the most difficult to wet without surfactant but is impacted most by the addition of TTAB surfactant.

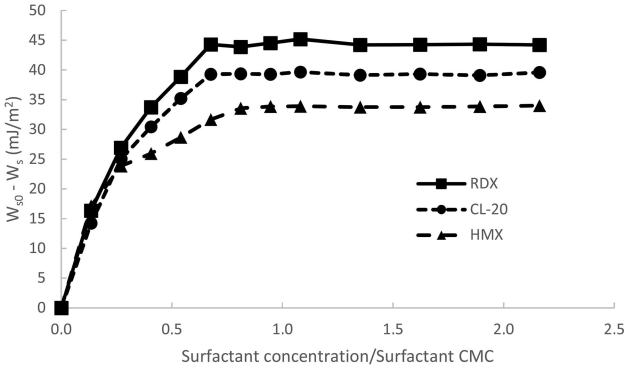


Figure 12. W_{s0}–W_s as a function of normalized surfactant concentration for TTAB solutions on RDX, CL-20 and HMX surfaces.

4 Conclusions

Wetting behavior of RDX, HMX and CL-20 surface using nonionic (Triton-X), anionic (SDS), and cationic (TTAB) surfactant solutions has been investigated by contact angle measurements. All three explosives showed smaller contact angles in the presence of surfactants before reaching a plateau. The addition of TTAB showed the largest decrease of contact angle compared to SDS and Triton-X. The liquid-vapor surface tension γ_{lv} was measured as a function of TTAB surfactant concentration in aqueous solutions and used to construct a Zisman plot to determine the critical surface tension of RDX, HMX and CL-20. The results showed that HMX displays the highest degree of wettability and RDX is most difficult to wet. The computed values of the work of spreading complement the previous results regarding the contact angle measurements and showed that RDX is most impacted by the addition of TTAB. The present wettability study plays an important role in the formation of well-wetted energetic surfaces needed for efficient wet milling, coating and granulation processes.

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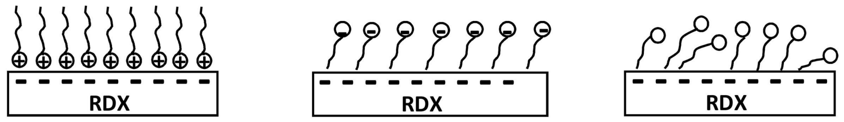

(a) TTAB (b) SDS (c) Triton-X

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