Chapter 6

STUDIES ON PREPARATION OF SPHERICAL PARTICLES OF FOX-7 USING MICELLAR NANO REACTOR
6.1 Abstract

The need and preparation of spherical 1,1-Diamino-2,2-dinitroethene (FOX-7) particles to meet certain special applications in high explosives and propellant formulation have been illustrated. Preparation of spherical FOX-7 particles by using micro emulsion technique have not been reported in the literature. In the present study, preparation of spherical FOX-7 particle has been described using the novel concept of micelle based nano-reactor. Micelle based nano reactors have been prepared using micro-emulsion of triton-X 100, Cyclohexane and water. Analysis of the experimental result revealed that, the particle size and shape of FOX-7 can be varied by changing water to surfactant molar ratio in micro-emulsion. Formation of spherical FOX-7 particles in the reverse micelle reactors have been described in the subsequent sections. It is observed that spherical particles of FOX-7 are formed within two hours in the micro-emulsion media. Spherical particles synthesised in this method are generally in the range of sub-micron to nano-range. Impact sensitivity ($h_{50}$) of the spherical particles by fall hammer method obtained is around 45 cm compared to regular synthesised FOX-7 (i.e.50±5 cm) without altering any change in friction sensitivity, i.e. 36 kg. Loadability of the explosive charges can be enhanced by using spherical particles of FOX-7.

6.2 Introduction

FOX-7 is a futuristic insensitive high explosive and a potential candidate to replace RDX. Due to its chemical and thermal stability, it has created significant interest in recent past. FOX-7 is a new explosive ingredient with significant potential for application in high performance, insensitive munition (IM)-compliant explosive compositions. FOX-7 is prepared by
adopting a batch process by nitration of 2-methyl-4,6-dihydroxypyrimidine (MDP) to get FOX-7. Morphology of this material shows a hexagonal layer type crystal structure. However, it was essential to know whether spherical morphology of FOX-7 can be synthesised for certain application as the sensitivity of solid explosive materials is closely related with particle size and shape. The requirement of higher value of impact sensitivity may be met with spherical particles with defined size. Particles tending to spherical shape in comparison to non-spherical (needles/plates) with the same mean particle size have the advantages like,

- Higher ratio of surface to volume
- Better free flowing properties
- Higher bulk density

This means the more spherical the outer shape of the particles, the higher weight proportion of solid energetic particles can be put in the formulation. Spherical particles, generally, can be formed via the dispersion of the liquid phase which then becomes droplets in continuous phase. Literature information revealed that various research activities are being carried out in order to produce spherical FOX-7 particles. Thomas Heintz et.al (1) prepared spherical ammoniumdinitramide (ADN) particles by emulsion crystallization using molten ADN (as disperse phase) and paraffin oil (as continuous phase). Waldemar et.al (2) attempted for spherodization of FOX-7 crystals by high degree of agitation of suspension of the non-spherical crystal in various solvents for six to seven hours at different temperature but the process produced crystals of similar shape where the sharp edges/corners become slightly rounded. Since, FOX-7 doesn’t have sharp melting point it will be preferred to prepare such
spherical particle either at the stage of formation of nucleation while hydrolysis of nitrated- pyrimidinedione, NMPD or during recrystallisation in suitable organic solvent by using the micelles/micro-emulsions. Micelles are formed through a self assembling process which represents tiny template/nano-reactor which are generally used for preparing nano-structured materials of desired size and shape with required functionalities and attributes. Using miceller nano reactor/micro emulsion, various experiments have been reported out (3) on nitration of phenol to synthesize ortho-nitrophenol with dilute nitric acid. However, there is no literature available to synthesise spherical FOX-7 particle/ nano particles of FOX-7 using any other concepts.

Hence, a feasibility study has been carried out to synthesise spherical particles of FOX-7 by using the concept of micelle based nano reactor. The basic aim was to design the experiments followed by conducting the same at laboratory level to prepare spherical particle of FOX-7 and analysis of data by various instrument techniques. As a outcome of this study, it is realized that spherical particles of FOX-7 can be synthesised using the concept of miceller based nano reactor. These spherical particle are generally in the range of submicron and nano range. Details of the study are described in the subsequent sections.

6.2.1 Design of Nano Reactor

Nano reactors have been designed using the concept of micelles. Micelles are formed using the surfactants. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic tail as well as hydrophilic head as given in Fig. 6.1a.
Surfactants are classified based on the nature of the hydrophilic group. Different types of surfactants considered during the design of microreactor are given below.

- **Anionic Surfactants:** The hydrophile is a negatively charged group, e.g., RC₆H₄SO³⁻ Na⁺ (alkylbenzene sulfonate).
- **Cationic Surfactants:** The hydrophile bears a positive charge, e.g., RNH₃⁺ Cl⁻ (salt of a long-chain amine).
- **Nonionic Surfactants:** The hydrophile has no charge, e.g., R(OC₂H₄)ₓ OH (polyoxyethylenated alcohol).
- **Amphoteric (Zwitterionic) Surfactants:** The molecule contains both a negative charge and a positive charge group, e.g., RN⁺H₂CH₂COO⁻ (long-chain amino acid).

A fundamental property of surfactants (surface-active agents) have been exploited is to form aggregates, known as micelles. The first-formed aggregates, just above the critical micelle concentration (CMC), are reported to be spherical in shape, and the concentration where they start to form is known as the critical micelle concentration. Besides, on the basis of arrangement of hydrophilic group i.e. towards centre and away from centre, two types of micelles, normal micelles and reverse micelles respectively were considered while designing the present experimental systems of nano reactors. These nano reactors provide a unique way for
development of special type of advance materials for wide variety of applications in electronics, photonics, biomedical and other areas also. Following are the type of nano-reactors.

- **Normal micelle Nano Reactor**: The oil-in-water micelle is called as normal micelle. Here oil acts as a dispersed phase and water acts as a continuous phase. The size of nano reactor by normal micelles can be varied from 100 nm to 20 μm. Schematic of normal micelle is shown in Fig. 6.1b.

![Fig. 6.1b Schematic of normal micelles](image)

- **Reverse Micelle Nano Reactor**: Reverse micelles are fine dispersions of water in organic solvent stabilized by a surfactant molecule. Reverse micelles provide an example of organized self assemblies of surfactants in solution and are most widely used as reaction media or templates for biomimetic synthesis of various inorganic nano-particles. The hydrophilic head and hydrophobic tail of surfactants in a polar solvent self assemble to give reverse micelles where the polar core contains the hydrophilic heads and the a polar shell the hydrophobic chains. The size
of nano reactor by reverse micelles can also be varied from 100 nm to 20 \( \mu \)m. Schematic of reverse micelle is shown in Fig. 6.1c.

These nano reactor can be solubilized in the core forming water-in-oil droplets (minimum 5 nm) which eventually become the water in oil microemulsion as the water content increases (5 to 100nm). So, the water to surfactant molar ratio has a decisive influence on the diameter of the reverse micelles. The aggregation number is typically in the range of 20 to 30, lower than in direct-micelles due to hydrophilic core. The shape can be spherical, rod-like or lamellar and it also depends on the concentration of surfactant, electrolyte, other additives, etc. The droplets undergo continuous collisions and exchange their contents. The shape of nanoparticles synthesized in reverse-micelles would normally be spherical unless some system specific special care is exercised. Microemulsions have been used to control the particle size of many inorganic and organic materials because they induce drastic changes in the reagent concentration and this can be particularly used for tuning the reaction rates (4-6). In a given composition (nature of oil and aqueous phase), the nature
of surfactant molecules determines the exchange rate through the
elasticity (or rigidity) of the surfactant shell or interface. So, in order to
prepare the spherical particles of FOX-7, design of spherical nano-
template have been produced by using selected surfactant and co-
surfactant which is discussed in the experimental section.

6.3 Experimental

6.3.1 Chemicals

Following chemical composition is used in the present study,

- Surfactant (Triton X-100)
- Cyclohexane (oil media)
- Co-surfactant (n-hexanol)
- Water
- Target nitrated-MDP

Triton X-100 (C14H22O(C2H4O)n)

It is a nonionic surfactant which has a hydrophilic
polyethylene oxide group (on an average it has 9.5 ethylene oxide
units) and a hydrocarbon lipophilic or hydrophobic group. The
hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl group.
The critical micelle concentration is 0.22 – 0.24 m mole/lit. It is
often used as a surfactant along with suitable co-surfactant for the
preparation of reverse micro-emulsion to generate the nano
particle. It is also used in biochemical applications to solubilize
proteins. The structure of triton X-100 is as shown in Fig. 6.1d.

\[
\text{H}_3\text{C} - \text{C} - \text{CH}_2 - \text{C} - \text{CH}_3
\]
\[
\text{CH}_3 \quad \text{CH}_3
\]
\[
\text{CH}_3 \quad \text{CH}_3
\]
\[
(\text{OCH}_2\text{CH}_2)_x\text{OH}
\]

Fig. 6.1d. Chemical structure of Triton X-100
Cyclohexane (oil phase)

Cyclohexane acts as oil phase (continuous phase) for the preparation of reverse micro-emulsion. It is reported that the chain length of continuous oil phase can influence the properties of an interface through a surfactant chain-oil interaction. The longer is the chain length of oil, more difficult is the penetration into surfactant tail and hence there is a tendency to align itself parallel to the surfactant tail. Such alignment increases the inter-micellar exchange rate and as a result size of particle decreases.

n-Hexanol (co-surfactant)

n-Hexanol used as a co-surfactant (medium-chain alcohol) for the preparation of reverse micro-emulsion. The driving force for micro-emulsion formation is the low interfacial energy which is over compensated by the negative entropy of dispersion term. The low interfacial tension is produced by combination of two suitable molecules for example surfactant and co-surfactant. The addition of hydrophilic or lipophilic polar compounds (co-surfactants) can also change the hydrophilic or lipophilic character of the system, its solubility of water or oil, and the interfacial tension.

6.3.2 FOX-7 by Normal Synthesis method

Synthesis of FOX-7 has been carried out by nitration of MDP followed by hydrolysis of nitrated derivative. Nitration of MDP is highly exothermic reaction where a mixture of concentrated sulphuric acid, H$_2$SO$_4$ and nitric acid, HNO$_3$ are used as nitrating agent. MDP was dissolved in H$_2$SO$_4$ and HNO$_3$ acid was added slowly into it at a mole ratio of MDP : HNO$_3$ : H$_2$SO$_4$ :: 1 : 5.1 : 10.1 and the temperature was maintained at the desired level. After completion of each run, the reaction mixture was quenched into the cold water followed by
hydrolysis under high speed of agitation to get the product, FOX-7 which was then filtered, washed with water (till removal of acid) to separate the solid product. Scheme for synthesis of FOX-7 of regular particle size is given in Fig. 6.2.

Fig. 6.2 Block diagram for preparation of FOX-7 of regular particles

6.3.3 Spherical FOX-7 Particles using Micro-emulsion method

Micro-emulsion solution was prepared by using 52 wt% of cyclohexane as oil phase, 22 wt% of Triton X-100 as surfactant, 11 wt% of n-hexanol as co-surfactant. Surfactant to co-surfactant ratio used was about 2:1 by weight along with 15 wt% aqueous phase. Surfactant with co-surfactant was added first to
cyclohexane as the oil phase followed by addition of aqueous phases and then stirred at room temperature till an optically clear and stable reverse micro-emulsion obtained. To this micro-emulsion, nitrated intermediate of MDP was added slowly under vigorous stirring maintaining the temperature of about 25°C. The micro-emulsion containing nitrated MDP were kept for 2 hrs under vigorous agitation and then allowed to settled for 12 hrs. The precipitated powders were recovered/ separated by centrifuge followed by washing with acetone and methanol. The separated FOX-7 material then dried in a vacuum oven at 70°C for 16 hrs. The schematic diagram to prepare spherical FOX-7 particle using reverse micro-emulsion method is shown in Fig. 6.3.

Fig. 6.3 Synthesis of Spherical FOX-7 particles using micro-emulsion.
### 6.4 Results and Discussion

Details of experiments using micro-emulsion is shown in Table- 6.1

Table 6.1 Details of batches carried out by reverse microemulsion

(Cyclohexane : 156g  Triton X-100: 66 g, n-hexanol: 33g).

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>Wt of Intermediate (g)</th>
<th>Wt of water (g)</th>
<th>water/surfactant ratio</th>
<th>FOX-7 weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCN-1</td>
<td>96</td>
<td>9.18</td>
<td>5</td>
<td>Product not formed</td>
</tr>
<tr>
<td>MCN-2</td>
<td>96</td>
<td>18.36</td>
<td>10</td>
<td>0.19</td>
</tr>
<tr>
<td>MCN-3</td>
<td>96</td>
<td>27.54</td>
<td>15</td>
<td>0.6</td>
</tr>
<tr>
<td>MCN-4</td>
<td>96</td>
<td>36.72</td>
<td>20</td>
<td>1.18</td>
</tr>
<tr>
<td>MCN-5</td>
<td>96</td>
<td>45</td>
<td>24.5</td>
<td>2</td>
</tr>
<tr>
<td>MCN-6</td>
<td>96</td>
<td>55.08</td>
<td>30</td>
<td>2.93</td>
</tr>
<tr>
<td>MCN-7</td>
<td>96</td>
<td>100</td>
<td>54.5</td>
<td>3.2</td>
</tr>
<tr>
<td>MCN-8</td>
<td>240</td>
<td>150</td>
<td>81.7</td>
<td>8</td>
</tr>
</tbody>
</table>

It is seen from the above table that as the water to surfactant ratio goes on increasing, the yield of spherical FOX-7 goes on increasing. Spherical FOX-7 is then characterized by various analytical / instrumental methods. A mechanism proposed for the hydrolysis reaction in micro-emulsion is shown in Fig. 6.4.
It can be seen that after mixing of 2-diniromethylene-5,5-dinitropyrimidine-4,6-dione to reverse micro emulsion the hydrolysis of intermediate starts during the mixing process, Fig. 6.4.

The hydrolysis takes place inside the droplets (nucleation and growth) which control the final size of particles. This gives the homogeneous particle size distribution of FOX-7 nanoparticles. This is due to controlled hydrolysis in
reverse micro emulsion. The sizes of the micro emulsion droplets can be modified by varying the water to surfactant (R) ratio. The effect of water to surfactant molar ratio on the morphology of FOX-7 particles is seen to be one of the most important parameter, which determines the state of aggregation, size and morphology of the particles and nature of solubilized water molecules. The sample prepared in reverse micro-emulsion containing 15 wt.% aqueous phase (water/ surfactant molar ratio 25) shows nearly spherical particles with average particle size of 200 nm whereas the sample prepared in micro emulsion having water to surfactant molar ratio 30 shows spherical particle of FOX-7 with average particle size ~1 micron. The yield is around 30 %. This may be due to presence of less amount of water in reverse micro-emulsion. The characterization of as synthesised as well as spherical FOX-7 were confirmed by various analytical tools such as thermal analysis, nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, differential scanning calorimetry (DSC), scanning electron microscope (SEM) etc.

NMR spectroscopy reveals that FOX-7 is having two carbon atoms and four identical protons. In DMSO-D6 the single proton resonance for the amino protons occurs at approximately δ 8.8 ppm, shown in Fig. 6.6.

![Fig. 6.6. 1H NMR of FOX-7 / Spherical FOX-7](image)
$^1$H NMR spectrum of the FOX-7 sample gives a single of four hydrogen atoms of two amino groups with the chemical shift $\delta = 8.78$ ppm. Fig. 7 shows $^{13}$C NMR spectra to signals of carbon (C-1) with chemical shift $\delta = 128.1$ ppm and a single with chemical shift $\delta = 158.2$ ppm of carbon (C-2). The measured $^1$H and $^{13}$C NMR chemical shifts as identical with the literature reported values. $^{13}$C, $^{15}$N, spectra of FOX-7 were carried out with a Bruker AMX 360 spectrometer at 360.14, 90.57 and 36.50 MHz, respectively, at 25°C. For the measurement, the samples were dissolved in DMSO-d$_6$ and chemical shifts were referenced to the solvent signal ($\delta$ ($^1$H) = 2.55 ppm, $\delta$ ($^{13}$C) = 39.60, respectively.

The IR spectrum of DADNE was carried out on Shimadzu infrared spectroscopy (FTIR-8400) instrument. KBr was mixed with the sample. The powder was placed in the cup of diffused reflectance assembly and spectra were recorded. The infrared spectrum of FOX-7 shows absorbance in the ~3200-3400 and ~1350-1650 wave number range characteristic of the amino and nitro functionalities as well as numerous peaks in the fingerprint region (3), Fig. 6.8.
Thermal analysis of spherical FOX-7 samples was carried out in DSC. The DSC thermogram, Fig. 6.9 recorded at a heating rate of 10°C per minute showed major exothermal peaks at 283°C (maximum peak) and almost merging into a single peak. This is consistent with a two stage thermal decomposition. Additional minor ‘endothermic peaks’ were observed at 112-115°C and 165-172°C suggesting to thermally induced phase transition. So, thermal analysis provides further evidences of a two step processes of phase transition. No melting point is observed. The value of decomposition of both as synthesised and spherical FOX-7 are similar to the results reported in the literature. Besides, small variations in DSC spectrum of values from different batches of FOX-7 have recently been partially explained by OSTMARK et al. (7) by proposing relationship between particles size and the decomposing temperature.
Fig. 6.9  DSC thermo-gram of FOX-7

SEM image of as synthesised FOX-7 shows layer structure of rectangular rod shape crystal structure shown in Fig. 6.10.

Fig. 6.10  SEM Image of as synthesised FOX-7

The particle size was measured by using scanning electron microscopy (SEM Leica 440). SEM images of dried powders prepared by microemulsion method (by varying water to surfactant ratio) are shown in Fig. 6.11.
6.5 Conclusions

Nearly spherical particles of 1,1-diamino-2,2-dinitroethene (FOX-7) have been successfully prepared in reverse micro-emulsion of Triton X 100/cyclohexane/ water. The particle size and shape of FOX-7 can be varied by changing water to surfactant molar ratio in microemulsion. The method gives formation of FOX-7 particles within two hours. Spherical particles synthesised in this method are generally in the range of sub-micron and nano-range. Impact sensitivity ($h_{50}$) by fall hammer method is around 45 cm compared to regular synthesised FOX-7 (i.e. $50\pm5$ cm) without altering any change in friction sensitivity i.e. 36 kg. This may be explained as the particle size is reduced, surface area is increased, which makes the particles more active towards impact. Since, the layer structure of the crystal remains unchanged friction
sensitivity remains unaffected. The data collected during the study is helpful for scale-up the process in preparation of spherical particles.
6.6 References

1. Thomas Heintz, Indra Fuhr, 'Generation of spherical oxidizers particles by spray and emulsion crystallization', Fraunhofer ICT, Joseph-von-Fraunhofer-Str.7, 76327, Pfinztal (Berghansen), Germany.


