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# Preparation of Hexanitrohexaazaisowurtzitane (HNIW) Nano Particle by Normal Microemulsion Based Nonionic Surfactant

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***Abstract:***
*The behavior of nanoscale energetic materials is quite different from micronsized energetic materials in many ways. Recently, some techniques such as sol-gel method, high speed air impaction and vacuum co-deposition have been employed to obtain nanoscale energetic materials. However, only few attentions were paid to nanoscale energetic materials because of the fabrication difficulty. In this paper, the simple preparation of a nitramine 2,4,6,8,10,12 hexanitro 2,4,6,8,10,12 hexaazaiso wurtzitane (HNIW) with nanometer size by microemulsion method is presented. The microemulsion systems contained tween80, 2-propanol and n-butyl acetate as the oil phase. On the base of DLS measurement average particle size is 8 nm. The prepared nanoparticles are semispherical based on SEM picture.*
***Keywords:*** *Microemulsion, HNIW, Nanoparticle, Surfactant, Nonionic.*

## 1. INTRODUCTION

In the field of energetic materials, nano-structured components are of high importance for application because the sensitivity and performance are strongly changed when the size of the particles is reduced to nanometer-scale. By far the preparation of nano-energetic materials arouses the interest of scientists and engineers [1-5]. HNIW [2,4,6,8,10,12-hexanitro-2,4,6,8,10,12 hexaazaisowurtzitane] is a new explosive compound that has various military and commercial applications [6-8].
Size reduction of material has been done by different kind of methods to improve their properties [9-16]. A lot of work has been done on the preparation of nanometer-sized reactive powders. For example, RDX (cyclo-trimethylenetrinitramine), AP (ammonium perchlorate) pyrotechnics and other explosives with nanostructure have been prepared by sol-gel method. Also, nano-sized ammonium nitrate and RDX particles by a sublimation/ condensation process have been obtained [17-19].
A well-known method for the preparation of nanoparticles is solvent evaporation from an oil-in-water microemulsion. In this method, nanoparticles are prepared by dissolving the compound in a volatile water-immiscible solvent followed by emulsifying this solution in water. Solvent evaporation from the resulting microemulsion yields the formation of particles in a size range comparable to that of the emulsion droplets. The synthesis of inorganic particles in microemulsions is already widespread [20-22]. However, there are only a few reports on the formation of organic nanoparticles from microemulsions (nimesulde, propylparaben, celecoxib, griseofulvin, …) [23-27].
These studies have been extended to investigate the preparation of nanoparticle polycyclic nitramine

HNIW. The preparation of HNIW nanoparticle is carried out in microemulsion by drying microemulsion dispersion by lyophilizing.

## 2. EXPERIMENTAL

### 2.1. Materials and equipments

The starting material HNIW was synthesized by following the reported and paper procedures [29]. Other materials such as HNIW, 2-propanol, n-butyl acetate and ethyl acetate were used as received from Merck.

The drying process was carried out with using a Christ lyophilizer (model 2-4α). The size and shape of particle were observed under scanning electron microscope using a Philips XL30 series instrument using gold film for loading the dried particle on the instrument. The size measurement of particle in solution carry out by DLS (model zeta plus) in room temperature and wavelengths 957nm.

### 2.2. Preparation of microemulsion

All microemulsion solutions were prepared at room temperature by adding water to mixture of n-butyl acetate, ethyl acetate, tween80, 2-propanol and manually shaking until a transparent and thermodynamic stable system was obtained. Before microemulsion preparation, HNIW was loaded in n-butyl acetate or ethyl acetate. The resulting compositions were equilibrated for 24h at 25°C. Only compositions that remained transparent and homogeneous after this period of time were attributed as limpid and thermodynamic stable microemulsion. All formulation for microemulsion preparation is represented in table 1.

### 2.3. Converting microemulsion to nanoparticles

Freezing microemulsion dispersion was done by liquid nitrogen and then dried. The drying process was carried out at temperature of –36°C and absolute pressure <1 mbar. The drying process continues for 18 hours. Ultimately all solvents evaporate and mixture of tween80 and HNIW nanoparticles was resulted.

## 3. RESULTS AND DISCUSSION

### 3.1. Evaluation of organic solvent nature

Two organic solvents consist of n-butyl acetate and ethyl acetate were applied to elucidate effect of solvent nature in preparation of microemulsion. Some physical properties of this solvent has been studied; such as percentage of miscibility in water and evaporation rate. Ethyl acetate has higher miscibility in water. Therefore it would exist in water phase of microemulsion. Also it has higher evaporation rate rather than n-butyl acetate so it is difficult to prepare limpid and thermodynamically stable microemulsion.

As a result, limpid and thermodynamic stable microemulsion was obtained, only with applying n-butyl acetate as organic solvent. In order to evaluate the n-butyl acetate proportion in microemulsion formulation, different ratios of (tween80 + 2-propanol) to n-butyl acetate for preparation of microemulsion were applied (2:1, 3:1, 4:1). Justly microemulsion in 4:1 ratio was limpid and thermodynamically stable.

### 3.2. Evaluation of co-surfactant and surfactant nature

2-propanol was selected as the short chain alcohol

***Table 1:*** *All Formulation for microemulsion preparation*

| entry | n-butyl acetate: HNIW (w/w) | (2-propanol+tween80) : oil phase (w/w) | Tween80 : 2-propanol (w/w) |
|---|---|---|---|
| (1) | 5:1 | 2:1 | 2 :1 |
| (2) | 5:1 | 3:1 | 2.5:1 |
| (3) | 5:1 | 4:1 | 3:1 |

that would further reduce the critical packing parameter and the rigidity of tween80 interfacial film, allowing it to have the sufficient flexibility required to form microemulsions. 2-propanol has an evaporation rate similar to n-butyl acetate but lower than ethyl acetate and its aqueous solubility is low compared to the shorter chain alcohols.

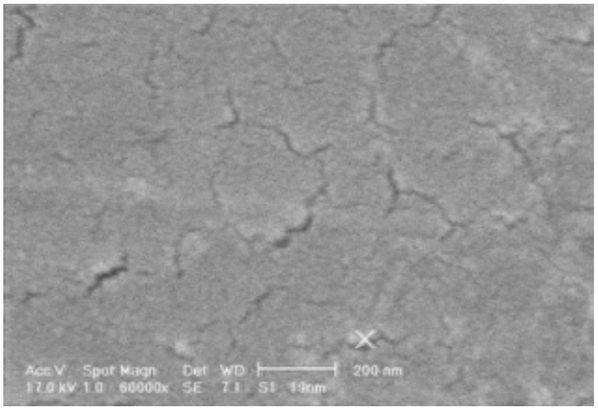


***Figure 1:*** *SEM Image of HNIW for entry (1)*

Due to those properties, it is expected that 2-propanol will be mostly located at the droplet interface rather than at the aqueous phase of the microemulsion. During the evaporation process, this alcohol should evaporate at a rate similar to the n-butyl acetate, but lower rate than ethyl acetate and instantly forming oil-free nanoparticles. Different ratios of tween80 to 2-propanol for preparation of microemulsion were applied (2:1, 2.5:1, 3:1). In ratios of 2.5:1 and 3:1, limpid and thermodynamically stable microemulsion was obtained. This indicates that for preparation of microemulsion with non ionic surfactant, high percentage of surfactant is needed.

### 3.3. HNIW nanoparticle formation and characterization by SEM and DLS

In order to evaluate the size of nonaparticles prepared in different limpid microemulsion, two formulations for drying have been chosen. They are represented in table 2.

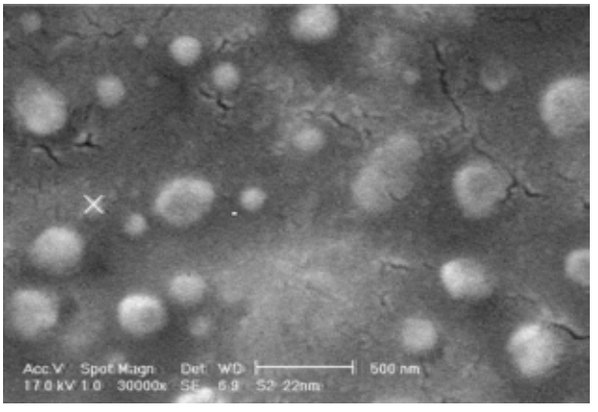


***Figure 2:*** *SEM Image of HNIW for entry (2)*

The nanoparticles were observed by SEM and images are represented in Figure 1 and Figure 2. Also, the sizes of nanoparticles in solution have been measured by DLS analysis and their distribution diagrams are represented in Figures 3 and 4. It is significantly obvious that by decreasing the ratio of tween80 to 2-propanol from 3:1 to 2.5:1, average particle size increases from 8 nm to 70 nm on the base of DLS analysis.

In both formulations, particles are semispherical on the base of SEM images. This result could stem from microemulsion structure; where of normal microemulsion formulation contains high percentage of surfactant and low percentage of

***Table 2:*** *Chosen Formulation for freeze drying step*

| entry | Particle size (nm) | tween80 : 2-propanol (w/w) | (tween80 + 2-propanol) : n-butyl acetate (w/w) |
|---|---|---|---|
| (1) | 8 | 3:1 | 4:1 |
| (2) | 70 | 2.5:1 | 4:1 |

alchohol, so by increasing alcohol percentage, micelles inflate and particle sizes increase.

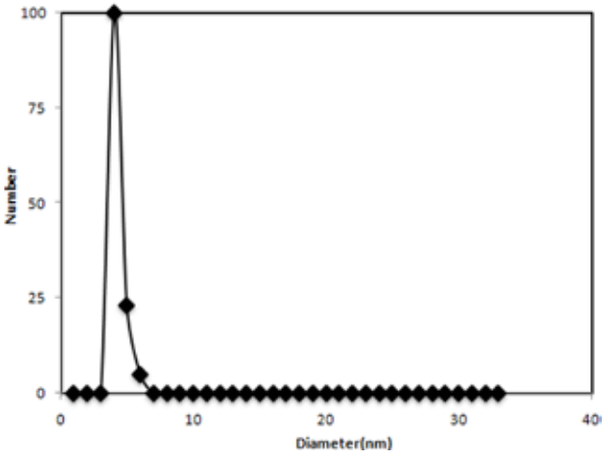


***Figure 3:*** *Particle size distribution by DLS analysis of HNIW for entry (1)*

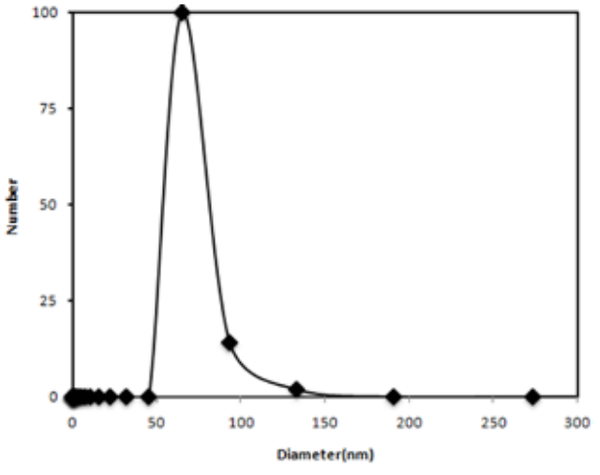


***Figure 4:*** *Particle size distribution by DLS analysis of HNIW for entry (2)*

## 4. CONCLUSION

For energetic materials, a safe and high performance size reduction method such as microemulsion is required. The microemulsion technique led to successful fabrication of HNIW nanoparticle with using n-butyl acetate as organic solvent. Applying ethyl acetate as organic solvent, did not obtain limpid and thermodynamic stable microemulsion. This problem stems from high miscibility of ethyl acetate in water and its higher evaporation rate. Limpid and thermodynamically stable microemulsion just by applying ratio 4:1 of (surfactant + co-surfactant) to n-butyl acetate and ratios 2.5:1 and 3:1 of surfactant to co-surfactant was obtained. By decreasing ratio of "surfactant to co-surfactant" from 3:1 to 2.5:1 average particle size increases from 8 nm to 70 nm.

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