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Statistical Optimization of the Preparation of HNIW Nanoparticles via Oil in Water Microemulsions

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Abstract: HNIW (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) is a family member of high-energy density cage nitramines which have so many versatile applications. In this paper, HNIW nanoparticles were prepared by the oil in water microemulsion route. The effects of various experimental parameters on this reaction were investigated using the Taguchi method. The effects of different variables: organic phase, water/organic phase (W1/W2), organic phase/propanol (W3/W4) and HNIW weight percent, on the particle size of the HNIW were investigated at three distinct levels. Optimal conditions for obtaining HNIW nanoparticles were determined. Performing the process under the optimal conditions proposed by the Taguchi method leads to the production of HNIW nanoparticles with an average size of about 80 nm. The HNIW nanoparticles were characterized using Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS), Differential Thermal Analysis (DTA) and X-Ray Diffraction (XRD).

Keywords: HNIW, microemulsion, surfactant, nanoparticle, parameter optimization

1 Introduction

The search for new energetic materials as potential replacements for the currently used explosive and propellant formulations (used in gun and rocket propellants)

is an area of intense investigation into military and industrial applications [1-3]. 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW, Figure 1) is one of the most interesting energetic molecules to be developed in recent years. The synthesis of HNIW has been discussed in many articles, and several precursors for the preparation of HNIW have been described [4-6].

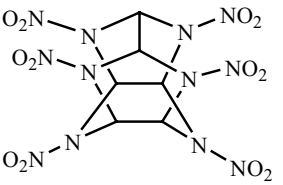


Figure 1. Chemical structure of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW).

Nielsen and co-workers reviewed many of the chemical and physical characteristics of HNIW in a recent article [6]. The properties of micronized and nano-sized energetic materials have been presented in many articles [7, 8]. Nano-structured energetic components have high importance for application because the sensitivity and other characteristics are strongly changed when the size of the particles is reduced to the nanometer-scale. Various methods have been used to prepare fine particles, such as grinding, crystallization, spray freezing into liquid nitrogen, wet and jet milling, spray drying, and supercritical fluids, but these methods have many disadvantages [9]. The greatest shortcoming of these methods is the requirement of high temperature to evaporate the solvent, difficulty in controlling the particle size and broad particle size distribution, and limitations for scale up and safe processing [10-12]. The microemulsion procedure is one of the most effective, flexible and convenient methods for producing nanoparticles with a minimized degree of agglomeration and controlled morphology. These systems are optically transparent, well characterized, thermodynamically stable and easily manufactured, consisting of nano-sized cages for the preparation of nano-particles. Although the preparation of inorganic particles in microemulsions is already widespread, only a few organic nanoparticles have been synthesized in microemulsion media [13-20].

One of the well-developed techniques for optimizing the experimental conditions is the application of experimental design. Taguchi is a well-known method of experimental design. The Taguchi method has been developed by G. Taguchi. It can provide a simple, efficient, and systematic approach, to optimize the designs for performance, quality, and cost. Therefore, it is a powerful tool in the design of experiments [21-26].

The Taguchi method, as with other simultaneous optimization techniques, has a previously planned array of experiments. In these methods, collection of the results and determination of the optimum conditions are carried out by constructing the response surface or by retention mapping [27]. The designed arrays in the Taguchi method are used to assign some variables to a series of experimental combinations, and the results obtained can be analyzed by common mathematical procedures [28, 29]. It is notable that the Taguchi method can separate the effects of different parameters with the aid of data obtained via performing the experiments according to the proposed orthogonal arrays [30-33]. Consequently, many academic research groups have used the Taguchi Robust for statistical optimization [34-36]. In this paper, we report a method for the preparation of HNIW nanoparticle by applying the oil in water microemulsion technique. Furthermore, the Taguchi Robust Design was used for optimizing the preparation of HNIW nanoparticles and evaluating the effect of parameters on the particle size of the HNIW produced. The aim of the application of the Taguchi method is to decrease the number of experiments and to aid visualization of the effects of all parameters on the experiments. The Taguchi Robust has a design of a L9 orthogonal array. The four experimental parameters include the organic phase, water/organic phase (W1/W2), organic phase/propanol (W3/W4) and HNIW weight percent, at three different levels.

2 Experimental

2.1 Materials and instruments

HNIW was prepared by nitration of 2,4,6,8,10,12-tetraacetyl 2,4,6,8,10,12-hexaazaisowurtzitane (TAIW) in our research laboratory, according to the conventional method [37]. Cetyl trimethyl ammonium bromide (CTAB) as a cationic surfactant, 2-propanol as a co-surfactant, and n-butyl acetate, isobutyl acetate and ethyl acetate as a suitable organic solvents were purchased from Merck (Darmstadt, Germany). The lyophilizing process was performed by a Christ lyophilizer (model 2-4α). Double-distilled deionized water was used for the preparation of all microemulsions. The morphology and size of the nanoparticles were observed by scanning electron microscopy (SEM, Philips XL30) after gold film coating. A Heraeus (RF model) centrifuge was used for the precipitation process. The size measurement of the particles in solution was carried out using dynamic light scattering (model zeta plus) at room temperature and wavelength 957 nm. The thermal properties of the nanoparticles were evaluated by differential thermal analysis (DTA, Bahar STA-503). X-ray diffraction (XRD) data were recorded

on a D/max 2500 (Japan, Rigaku) diffractometer with monochromatized Cu Kα radiation at 40 kV and 40 mA. The samples were packed into a vitreous holder and scanned from 2 to 50° (2θ), increasing in increments of 0.02° every second.

2.2 Procedure

Typical procedure for microemulsion preparation: HNIW (1 g) was dissolved in n-butyl acetate (8 g) with gentle stirring at room temperature to form the organic phase, then CTAB (3 g) as a surfactant, 2-propanol (15 g) as a co-surfactant and water (24.5 g) were added and manually shaken until formation of the microemulsion dispersion had occurred. In the second step, the microemulsion was lyophilized. In the lyophilizing step all of the solvent was removed from the frozen microemulsion. The resultant solid is a mixture of the surfactant and HNIW nanoparticles. The surfactant was separated from the HNIW nanoparticles by washing the mixture several times with water as follows: deionized water (10 mL) was added to the powder (1 g) obtained from the lyophilization step. It was then stirred manually until all of the surfactant had dissolved in the water. By centrifuging the suspension, all of the HNIW nanoparticles were precipitated. The water was decanted, and the HNIW nanoparticles were dried at 50 °C during 48 h. HNIW nanoparticles (0.08 g) were obtained.

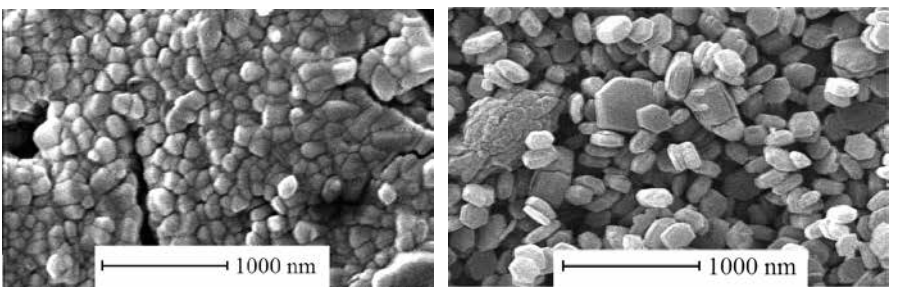
3 Results and Discussion

3.1 Influence of the components in microemulsion preparation

In order to find the operational conditions of the microemulsion formulation, the experimental design was applied for the preparation of HINW nanoparticles. It is notable that in the first step some primary experiments have to be done to find the factors and levels for the experimental design. As shown in Table 1, four experimental parameters, including the organic phase, water/organic phase (W1/W2), organic phase/propanol (W3/W4) and HNIW weight percent were studied at three different levels by the L9 orthogonal array proposed by the Taguchi Robust Design. The effect of three solvents, n-butyl acetate, isobutyl acetate and ethyl acetate, was studied as the organic phase in the microemulsion formulation. The parameters investigated and their tested levels in each experiment are presented in Table 1. SEM images of two micronized HNIW samples from different operational conditions are shown in Figure 2. The particle sizes of these two entries have the greatest differences, but the images of other entries are similar to these, with small differences. The last column of Table 1 gives the average particle size of the HNIW samples prepared under the operational conditions of each experiment.

Table 1. Assignment of the factors and levels in the experiments by using an Orthogonal Array (3^4) matrix and the average particle sizes of the HNIW produced as a response

Entry	Organic phase	Water/ organic phase	Organic phase/ propanol	HNIW wt.% in organic phase	Result [nm]
1	n-butyl acetate	1/2	1	2.5	163
2	n-butyl acetate	1/3	3/2	2	125
3	n-butyl acetate	1/4	2	1.5	94
4	ethyl acetate	1/2	3/2	1.5	211
5	ethyl acetate	1/3	2	2.5	238
6	ethyl acetate	1/4	1	2	215
7	isobutyl acetate	1/2	2	2	108
8	isobutyl acetate	1/3	1	1.5	145
9	isobutyl acetate	1/4	3/2	2.5	172



(a) (b)

Figure 2. SEM images of HNIW particles obtained by different runs of the Orthogonal Array 9 (Table 1) via the microemulsion method: (a) entry 3, (b) entry 5.

Statistical optimization by the Taguchi Robust Design, when there is no interaction between the variables, is included in three known steps as follows: (1) determination of the optimal operation conditions for the procedure investigated; (2) investigation of the individual effect of any studied variable in the response, which in the present study was the average particle size of the HNIW samples prepared; and (3) estimation of the response to the process under the optimum conditions determined in step one. Therefore, the first step was to determine the influence of each parameter, at any investigated level, on the particle size of the HNIW samples prepared via the microemulsion method, by combining the responses of all experiments in which a parameter was tuned at the

same level, then dividing this by the number of trials performed at the same level. In this way, the effect of all four parameters in 9 experiments has been evaluated. Figure 3 presents the curves obtained corresponding to the HNIW particle sizes for each level of the parameters investigated. The graphs show the variations in the average particle size of the HNIW caused by changing the level of the investigated variables. Analysis of variance (ANOVA) was performed for the experimental data obtained (average particle size of the micronized HNIW obtained via the microemulsion method). Table 2 presents the ANOVA results for the effects of the parameters investigated by the micoemulsion method at three different levels. As can be seen in this table, at the confidence level of 90%, except for the water/organic (W1/W2) phase, the other variables, the organic phase, organic phase/propanol (W3/W4) and HNIW weight percent, have significant effects on the particle size of the HNIW micronized via the microemulsion method.

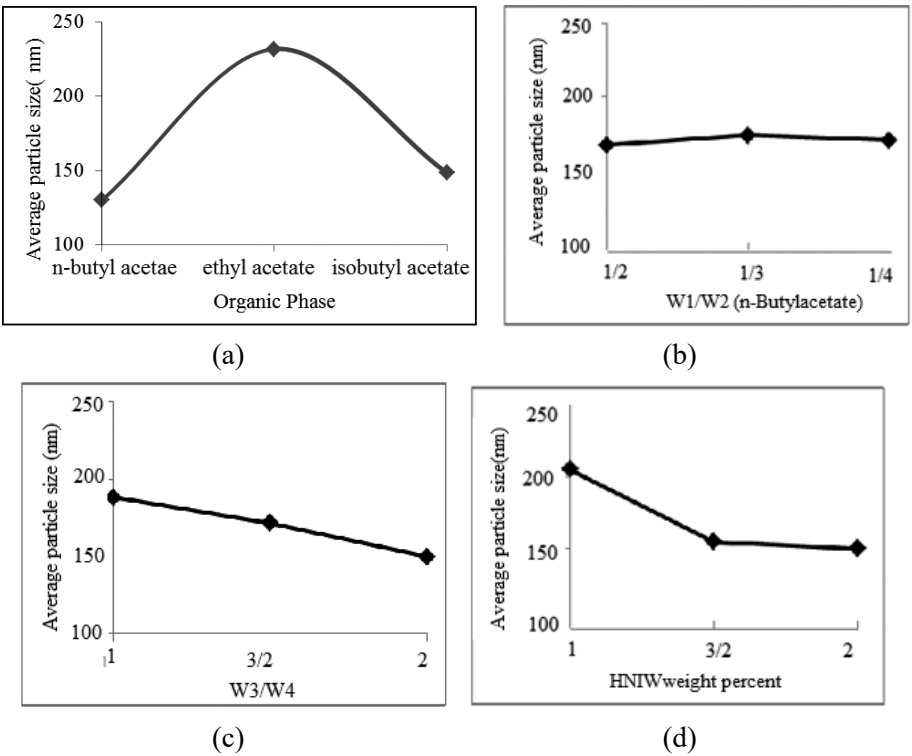


Figure 3. Effects of the level of variation for the process parameters studied on the average size of the HNIW particles: (a) organic phase (n-butyl acetate); (b) water/organic phase (W1/W2); (c) organic phase/propanol (W3/W4); (d) HNIW weight percent.

The ANOVA data showed that the weight ratio of water/organic phase (W1/W2) plays no significant role in the investigated levels for controlling the size of the HNIW particles. However, the nature of the organic phase has the most significant role in particle size tuning and amongst the levels studied (n-butyl acetate, ethyl acetate and isobutyl acetate), n-butyl acetate showed the best efficiency. This may be attributed to the physicochemical properties of n-butyl acetate. One of the other studied parameters was the HNIW weight percent; the best level for this factor is 1 percent. The reason for the best result in the application of 1 wt.% HNIW originates from the solubility of HNIW in the organic phase. Additionally, three different weight ratios of organic phase/propanol (W3/W4) (1, 3/2, and 2) were investigated and our finding showed that the best level for this parameter was 1, in other words, equal proportions of organic phase and propanol.

Table 2. ANOVA results for the procedure optimization for the micronization of HNIW by an Orthogonal Array $9\cdot(3^4)$ matrix

Factor	DOF[a]	S	V	Pooled[b]			
				DOF	S′	F′	P′
Organic phase	2	15388.2	7694.1	2	17616.7	98.5	75.2
Water/organic phase (W1/W2)	2	156.2	78.1	-	-	-	-
Organic phase/ propanol (W3/W4)	2	13042	652.1	2	2216.7	8.5	5.7
HNIW percent	2	3417.5	1708.8	2	5550	21.9	16.1
Error	2	156.2	33.3	2	66.7	-	3.1

[a] Abbreviations: DOF: degrees of freedom; S: standard deviation; V: variance; S′: standard deviation after pooling; F′: calculated value for the F test; P′: participation of each factor on the result after pooling.
[b] The critical value was at 90% confidence level.

3.2 Preparation of HNIW nanoparticles under the optimum conditions of the microemulsion method

As proposed by the ANOVA data and considering the average effect of each parameter (Figure 3), the optimum conditions for micronization of HNIW by the microemulsion method include: use of n-butyl acetate as the organic phase, a weight ratio of 1 for the organic phase/propanol (W3/W4) and 1 weight percent of HNIW. Thus, the particle size of HNIW produced by the microemulsion method under these optimum conditions can be estimated using the following expression [38]:

$$Y_{opt} = \frac{T}{N} + \left(P - \frac{T}{N} \right) + \left(F_{sol} - \frac{T}{N} \right) + \left(S_{Nature} + \frac{T}{N} \right) + \left(SUR_{type} - \frac{T}{N} \right)$$

where T/N is average particle size of the HNIW produced over all of the 9 experiments plus contributions from F_{sol}, S_{Nature} and SUR_{type}, at the level which produced the minimum particle size calculated from the average effect of each factor (Figure 3); while T is the overall value of the HNIW particle size in all runs in Table 1, N is the total number of experiments, Y_{opt} is the size of the HNIW particles under the optimum conditions, P, F_{sol}, S_{Nature} and SUR_{type} are the calculated average sizes of HNIW particles at the optimum levels of pressure, HNIW solution feed rate, type of solvent and type of surfactant, respectively. The results of particle size estimation for HNIW prepared under optimum conditions at 90% confidence level, will have an average particle size of about 90 nm. In the next stage of this work, HNIW nanoparticles were prepared under the optimum conditions generated by ANOVA. A SEM image for HNIW nanoparticles produced under the optimum conditions is shown in Figure 4. A diagram of the particle size distribution is given in Figure 5. The average size of HNIW particles obtained under these optimum conditions is about 80 nm.

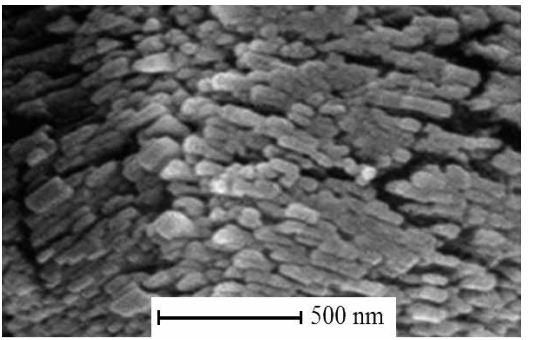


Figure 4. SEM image of HNIW nanoparticles.

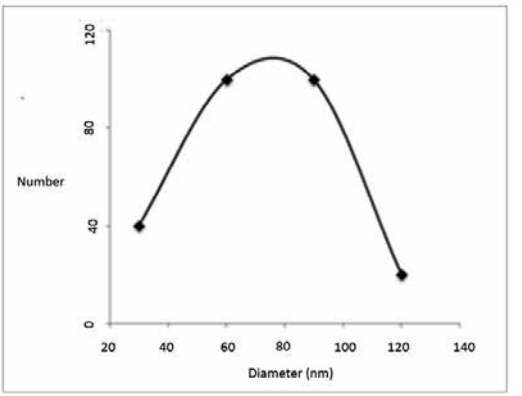


Figure 5. Particle size distribution.

3.3 Characterization of nanoparticles by dynamic light scattering

Measurement of the nanoparticle sizes in solution was done by dynamic light scattering (DLS) analysis. The purpose of this analysis was the evaluation of the nanoparticle sizes in solution and the measurement of the inclination of the nanoparticles to aggregate. The diagram is shown in Figure 6. The average particle size obtained, based on this analysis, was 225 nm. The difference in the average-size observed by SEM and DLS stems from the fact that nanoparticles immediately aggregate in solution.

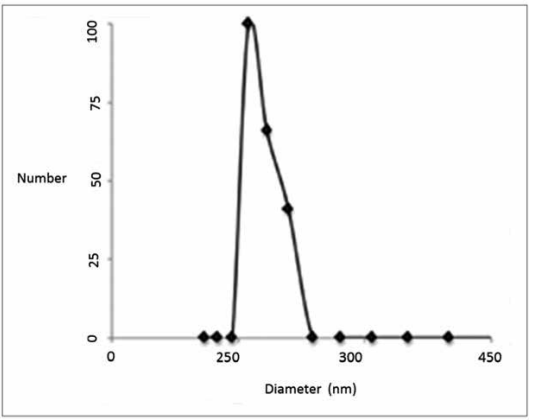


Figure 6. Particle size distribution by DLS analysis.

3.4 Nanoparticle characterization by DTA

One of the most important aspects in the study of energetic materials is their thermal properties. Thermal analysis of the nanoparticles after surfactant separation was studied by DTA. Figure 7 shows the DTA analysis curve. The curve shows a single sharp peak. This curve also indicates that the decomposition point of the nanoparticles is in agreement with the decomposition point of HNIW, and shows that size reduction does not affect the thermal properties based on literature values [39, 40]. Furthermore, this curve shows that the nanoparticles are pure.

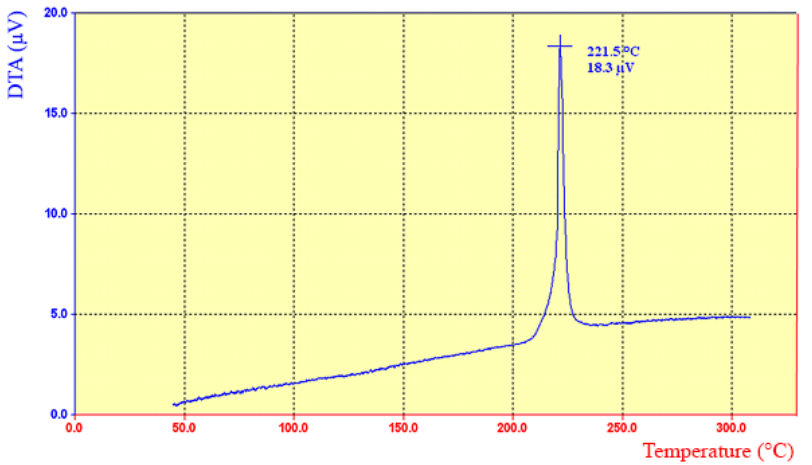


Figure 7. DTA analysis of HNIW nanoparticles; sample mass (5 mg), heating rate (10 °C·min^{-1}), Atm. air.

3.5 Nanoparticle characterization by XRD

There are four polymorphs of HNIW crystals (α-, β-, γ-, and ε-forms). The different crystalline forms have different densities and sensitivities. Figure 8 shows the X-ray Diffraction of the HNIW nanoparticles. Based on literature data, this pattern indicates that the nanoparticles exist in the β polymorph [41].

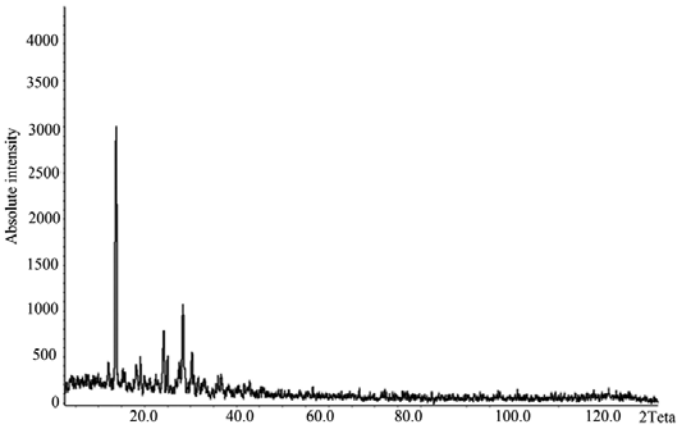


Figure 8. XRD pattern of HNIW nanoparticles after surfactant separation.

4 Conclusion

In summary, HNIW nanoparticles were prepared by the oil in water microemulsion method. In this study, various factors that effect the limpid and thermodynamic stability of microemulsion formation were optimized. Optimization of the experimental microemulsion method for micronization of HNIW was carried out statistically with the aid of the Taguchi Robust Design. The studies on various parameters illustrated that the nature of the organic solvent has the most significant effect on microemulsion formation. n-Butyl acetate as an immiscible organic solvent performs better than the other organic phases studied. The weight ratio of water/organic phase (W1/W2) plays no significant role at the investigated levels. The percent contribution of two other factors, organic phase/propanol (W3/W4) and HNIW weight percent was 5.7 and 16.1, respectively. Under the optimum conditions for the microemulsion method proposed by the Taguchi method, β-HNIW nanoparticles with an average size of 80 ± 10 nm were prepared.

5 References

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