Statistical Optimization and Selective Separation of RDX and HMX Explosives by Using Binary Solvent Mixtures Containing Ethyl Acetate and Water

Sajjad Damiri,* Hamid Reza Pouretedal, Hadi Panahi, Abdollah Dris

Department of Applied Chemistry, Maleke-ashtar University of Technology, Shahin-shahr, Esfahan, I. R. Iran
*E-mail: s_damiri@mut-es.ac.ir

Abstract: The present study introduces the application of a binary solvent of ethyl acetate and water for the selective separation of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). The effect of temperature and weight percent of ethyl acetate in water on the solubility of RDX and HMX over a temperature range of 273.15 K to 363.15 K and 70.0 wt.% to 100.0 wt.% ethyl acetate in water mixtures were modelled and optimized using a central composite design (CCD) and response surface methodology (RSM) in Minitab (ver. 16) software. Multiple regression analysis and analysis of variance (ANOVA) showed that the predicted results were in good agreement with the experimental data. The enthalpies of dissolution and mixing of the materials were determined experimentally from the solubility data. The experimental results showed that the solubility ratio of RDX to HMX can change 6.53- to 16.55-fold, indicating a much lower solubility of HMX in this binary solvent, for a relatively selective separation of RDX and HMX mixtures. Separation experiments under optimized conditions showed that 98.3% of the RDX impurity in HMX was recovered in the first precipitation with an HMX purity of > 99.5% as characterized by high performance liquid chromatography (HPLC).

Keywords: RDX and HMX, explosive, ethyl acetate, solubility, separation

1   Introduction

Octogen (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), commonly known as HMX (High Melting explosive), is the most powerful military explosive in current

use; however, the higher performance of HMX compared to RDX (Research Department explosive), 1,3,5-trinitroperhydro-1,3,5-triazine, is countered by its higher cost of production. This has restricted the use of HMX to the components of high performance propellants and powerful explosive compositions. HMX is produced mainly by the nitration of hexamethylenetetramine using the modified Bachmann method. Both HMX and RDX are produced from the same raw materials. Differences in the distribution depend on the proportions of reactants, sequence of feeding and temperature during synthesis [1, 2]. Two types of HMX used for military applications [3] are type A (maximum RDX content of 7.0 wt.%) and type B (maximum RDX content of 2.0 wt.%). A special grade of HMX having > 99.8% purity and offering thermally stable characteristics is used in well-perforating guns in the oil industry [4]. The concentration of RDX in crude HMX using the Bachmann method is usually 10.0% to 20.0%, although the HMX concentration will vary according to the manufacturing conditions.

The current solvents and separation techniques for the separation of RDX and HMX include cyclopentanone [5], acetonitrile [6] and dimethyl ether [7], acetone [8], and also the molecularly imprinted polymer solid phase extraction method [9]. Some studies have examined the solubility and crystallization of HMX in solvents such as DMF [10], binary compositions of γ-butyrolactone, dimethylsulfoxide and N-methylpyrrolidone with water [11]. The solubility of RDX has been tested in γ-butyrolactone, cyclohexanone, N-methylpyrrolidone and acetone with water as binary solvents [12]. Also, the crystallization of HMX has been studied in γ-butyrolactone [13], in the acetone/water system [14] and N-methylpyrrolidone, N,N-dimethylformamide (DMF) and propylene carbonate [15] solvents. The separation of RDX from HMX is relatively difficult because of the similar physical and chemical properties of the two compounds. The difference in the solubility ratio of RDX/HMX in conventional solvents such as acetone, DMSO and γ-butyrolactone, used to crystallize and purify these explosives, is less than 3-fold [6, 10]. Therefore, research on the selective separation of RDX and HMX using safe and low toxicity solvents is valuable.

Ethyl acetate (EA) solvent, which is naturally present in many organisms, has a relatively low risk of toxicity with a median lethal dose for rats (LD_{50}) of 5600 mg/kg [16]. The present investigation has tested the application of EA as a low toxicity solvent for the selective separation of RDX and HMX mixtures, to optimize the parameters affecting their solubility and to identify the best separation conditions. A central composite design (CCD) and response surface methodology (RSM) was developed using Minitab (ver. 16) [17]. Conventional methods vary only one parameter at a time; thus, the cumulative effect of all parameters cannot be studied. These conventional methods are also time-

consuming and require a number of experiments to determine the optimum levels, which makes them unreliable. RSM allows the interactions of two or more variables to be studied simultaneously. In addition, this method increases the yield, decreases the process variability, better confirms the nominal and target output responses and decreases the treatment time and cost [18].

2   Experimental

2.1 Materials and instrumentation

RDX and β-HMX with a purity of about 99.8% were obtained from the Iranian Defense industry. EA solvent of analytical grade purity (Sigma-Aldrich) and redistilled deionized water were used throughout. All extraction experiments were carried out in a laboratory-scale glass crystallizer (V = 500.0 mL) equipped with a water jacket, mechanical stirrer and two ground-glass joints connecting the crystallizer to a reflux condenser and a thermometer. The results of differential thermal analysis (DTA) of the products was recorded using a STA503 instrument (Bahr) in alumina crucibles. The DTA data was collected at 25-350 °C for 5.0 mg samples at a heating rate of 5 °C/min in an argon atmosphere. High performance liquid chromatography (HPLC) was carried out in a Shimadzu LC6A system equipped with a 6000 A pump and a Lambda-Max 481, LC spectrophotometric UV detector at 230 nm. A μ-Bondapak C18 125 Å column, 10 μm, 3.9×300 mm was used. The mobile phase was a 30/70 methanol/water mixture at a flow rate of 1.5 mL/min.

2.2 Measurement of RDX and HMX solubility in binary solvents

The solubility of RDX and HMX in the binary solvent mixtures of EA/water was measured by the isothermal method proposed by Kim *et al*. [11, 12]. The solubility for a given mixture was reproducible within 0.01 g of RDX or HMX per 100.00 g of solution.

2.3 Experimental design

Minitab 16.0 was used for the CCD, analysis of experimental data and optimization of the separation conditions for the two factors of temperature of the mixture (X_1) and the weight percent of EA in the solvent (X_2). The experimental design was applied at $20.0 \leq X_1 \leq 78.0$ °C and $70.0 \leq X_2 \leq 100.0$%, respectively, for a mixture load of 100 g. The CCD generated 14 runs for each RDX or HMX component, where the RDX solubility (Y_1) and HMX solubility (Y_2) in the EA/water mixtures was determined experimentally for each run prior to

modelling. Each experiment was repeated at least three times and the mean were applied for modelling. The designed conditions of the ingredients as defined by the software and the experimental results are shown in Table 1. The mathematical relationship of the responses Y_1 and Y_2 on the significant independent variables can be approximated by multiple regression and analysis of variance (ANOVA).

Table 1.   Central composite design for the determination of the solubility of RDX and HMX in 100 g EA/water solvent

Temperature [K/°C]	Ethyl acetate [wt.%]	Exp. Solubility of RDX (Y_1) [g/100 g]	Predicted Y_1 [g/100 g]	Exp. Solubility of HMX (Y_2) [g/100 g]	Predicted Y_2 [g/100 g]	Y_1/Y_2 ratio
293.1 / 20.0	85.00	1.43	1.59	0.10	0.11	14.30
301.6 / 28.5	74.39	2.30	2.07	0.19	0.18	12.11
301.6 / 28.5	95.61	1.82	1.68	0.11	0.11	16.55
322.1 / 49.0	70.00	3.25	3.32	0.30	0.31	10.83
322.1 / 49.0	85.00	3.32	3.28	0.49	0.48	6.78
322.1 / 49.0	85.00	3.25	3.28	0.48	0.48	6.77
322.1 / 49.0	85.00	3.21	3.28	0.48	0.48	6.69
322.1 / 49.0	85.00	3.25	3.28	0.48	0.48	6.77
322.1 / 49.0	85.00	3.18	3.28	0.47	0.48	6.77
322.1 / 49.0	85.00	3.20	3.28	0.49	0.48	6.53
322.1 / 49.0	100.00	3.28	3.24	0.28	0.29	11.71
342.6 / 69.5	74.39	5.84	5.58	0.57	0.55	10.25
342.6 / 69.5	95.61	6.05	5.87	0.62	0.61	9.76
351.1 / 78.0	85.00	6.85	7.05	0.72	0.73	9.51

2.4 Separation of RDX and HMX mixtures

Firstly, the HMX/RDX mixture (30.0 g, 20.0 wt.% RDX) was added to the EA/water mixture (200.0 g, 70:30). The mixture was heated to 75.0 °C and agitated for 60 min. Thereafter, the solution was cooled for 5.0 min under agitation to 70.0 °C, 50.0 °C or 30.0 °C. The solution was quickly vacuum-filtered through a fritted-glass 20 µm filter. The recovered solids were dried, weighed and analyzed by HPLC to determine the HMX purity.

3   Results and Discussion

3.1 Solubility of RDX and HMX

A series of experiments was carried out using the CCD (Table 1). The coefficients of the nonlinear full quadratic model for the solubility of RDX (Y_1) and HMX (Y_2) for any regime in the intervals in which the experimental design was modelled using the full quadratic models, as Equations 1 and 2:

$$Y_1 = 123.4051 - 0.7710\,X_1 - 0.2582\,X_2 + 0.001238\,X_1X_1 + 0.0007931\,X_1X_2 \qquad (1)$$

$$Y_2 = -11.9223 + 0.04427\,X_1 + 0.08382\,X_2 - 0.00007347\,X_1X_1$$
$$- 0.0008083\,X_2X_2 + 0.0001637\,X_1X_2 \qquad (2)$$

where X_1 is temperature (K), X_2 is weight percent of EA in the solvent (%), Y_1 is RDX solubility (g) and Y_2 is HMX solubility (g) in 100 g of the EA/water mixture.

The experimental results matched and validated the predicted values obtained using the models (Equations 1 and 2) reasonably well, at $R^2 = 99.17\%$ and adjusted $R^2 = 98.81\%$ for the response Y_1 with a standard deviation of 0.172, and $R^2 = 99.71\%$ and adjusted $R^2 = 99.53\%$ for the response Y_2 with a standard deviation of 0.0128. The residual plots in the models (not shown) indicated that the distribution of the residuals for the responses is approximately fitted normal and the residuals of the responses scatter randomly in the residual plots. ANOVA was also carried out for a 95% confidence interval to determine the statistical significance of the coefficients of the full quadratic model. F-values of 270.05 for Y_1 and 557.19 for Y_2 suggested that most of the variation in the response can be explained by the regression equations. Also, the p-values for the coefficients were > 0.05, which means that all terms in the regression equations have a significant correlation with the responses.

Figure 1 shows the 3D plots for the predicted responses based on the model functions used to study the effect of each factor on the solubility of RDX and HMX. The figure shows that increasing the mixture temperature and EA concentration increased the solubility of both RDX and HMX. Table 1 reveals that the solubility ratio of RDX to HMX can change from 6.53-fold to 16.55-fold. These results suggest a relatively selective separation by the binary EA/water solvent, which is environmentally friendly and has low toxicity, in the purification of RDX and HMX mixtures.
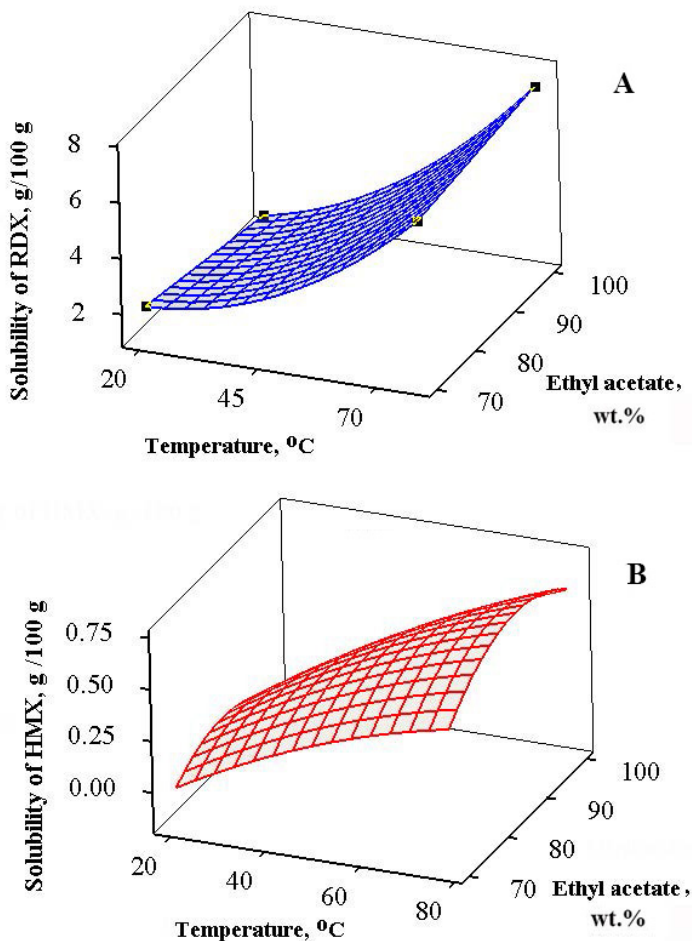
Figure 1. The three-dimensional (3D) plots for the solubility responses of RDX (A) and HMX (B) in the various temperatures and ethyl acetate/ water mixtures

Response optimization calculations were performed to determine the optimal mixture proportions for an increased RDX solubility (Y_1 response) and a decreased HMX solubility (Y_2 response). Response optimization recognizes a combination of input variable settings that jointly optimize a single response or a set of responses and generates a plot. Maximum responses of 6.06 g RDX per 100 g and minimum responses of 0.48 g HMX per 100 g of solvent were predicted for the 70.0% EA/water mixture at 73.3 °C with a mean desirability of prediction value of 0.8994. Desirability has a range of zero to unity. Unity

represents the ideal case; zero indicates that one or more responses are outside the acceptable limits. The solubility ratio of RDX to HMX was about 12.6-fold, which is a very suitable separation condition. Five replicate experimental tests similar to the separation method mentioned in Section 3.4 at the stated optimized conditions were performed for 30.0 g HMX containing 20.0% RDX. A product approaching 22.5 g HMX with a mean purity > 99.5% was obtained.

3.2 Activity coefficient, enthalpy of dissolution and enthalpy of mixing for RDX and HMX solubility

The solubility of RDX and HMX in the solvent mixtures was measured from 293.15 K to 351.15 K and the values are listed in Table 2. It can be seen that the solubility of RDX in EA is much higher than that of HMX and that the solubility of both explosives increased as the temperature is increased. It was observed that the solubility of HMX increased as the water content increased from 0.0% to 20% in the binary solvent, showing the synergistic effect of EA and water on amplifying the solubility of the explosives. It is known that crystallization of an explosive in the presence of water can remarkably ameliorate the safety problems associated with the use of organic solvents. The solubility data can be used to estimate the activity coefficients through the equilibrium relationship. If no solid-solid transition occurs in the considered temperature range, some useful simplifications can produce the following formula [12]:

$$ln x_1 \gamma_1 = \frac{-\Delta H_{fus,1}}{R} \left(\frac{1}{T} - \frac{1}{T_{m,1}} \right) \tag{3}$$

where x_1 is the mole fraction of component 1 (RDX or HMX) in the liquid phase, γ_1 is the activity coefficient of component 1 in the liquid phase, $\Delta H_{fus,1}$ is the molar enthalpy of fusion of component 1, $T_{m,1}$ is the melting temperature of component 1, T is the absolute temperature of the mixture, and R is the gas constant. The melting point and enthalpy of fusion $\Delta H_{fus,1}$ of HMX are 558.15 K and 70154.38 J/mol [11] and for RDX are 478.65 K and 35647.68 J/mol [12].

The activity coefficient γ_1 can be calculated using Equation 3 from the experimentally determined solution composition x and temperature T. Table 2 gives the mole fractions, equilibrium temperatures and activity coefficients of HMX and RDX according to the weight percent of EA in the solvent. To obtain the enthalpy of dissolution of RDX and HMX crystals in the solvent, Equation 3 can be altered to obtain Equation 4, which is obtained from the ideal solution theory [12]:

$$\ln x_1 = \frac{-\Delta H_{sol,1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,1}}\right) \tag{4}$$

where $\Delta H_{sol,1}$ is the enthalpy of dissolution and $T_{m,1}$ is the melting temperature of RDX or HMX. In an ideal system, $\Delta H_{sol,1}$ is equal to $\Delta H_{fus,1}$ and is obtained by assuming $\gamma_1 = 1$ in Equation 3 and $\Delta H_{fus,1} + \Delta H_{mix,1}$ for non-ideal systems.

Table 2. Mole fraction solubility and activity coefficient, enthalpy of dissolution and enthalpy of mixing for RDX and HMX explosives in ethyl acetate/water solvent

| Ethyl acetate [wt.%]	Temperature [K / °C]	Solubility [g/100 g]		$x_1 \times 10^3$		γ		$\Delta H_{sol,1}$ [J/mol]	$\Delta H_{mix,1}$ [J/mol]
		RDX	HMX	RDX	HMX	RDX	HMX		
100.0	313.1 / 40.0	2.05	0.18	6.61	0.44	1.3294	0.0167	29364.2 (R) 34217.1 (H)	-6283.5 (R) -35937.3 (H)
	323.1 / 50.0	3.10	0.30	9.96	0.73	1.3476	0.0230		
	333.1 / 60.0	4.00	0.43	12.82	0.10	1.5598	0.0352		
	343.1 / 70.0	5.70	0.63	18.17	1.53	1.6014	0.0503		
90.0	313.1 / 40.0	2.50	0.38	6.20	0.71	1.4173	0.0103	27193.4 (R) 17757.9 (H)	-8454.3 (R) -52396.5 (H)
	323.1 / 50.0	3.52	0.45	8.71	0.84	1.5416	0.0200		
	333.1 / 60.0	4.55	0.51	11.23	0.95	1.7806	0.0386		
	343.1 / 70.0	6.40	0.71	15.72	1.33	1.8504	0.0580		
80.0	313.1 / 40.0	2.60	0.42	5.24	0.64	1.6761	0.0114	26157.5 (R) 16138.3 (H)	-9490.2 (R) -54016.1 (H)
	323.1 / 50.0	3.07	0.52	6.19	0.79	2.1705	0.0213		
	333.1 / 60.0	4.20	0.56	8.44	0.85	2.3682	0.0432		
	343.1 / 70.0	6.30	0.75	12.61	1.14	2.3069	0.0676		
70.0	313.1 / 40.0	2.60	0.27	5.24	0.35	1.6761	0.0211	21584.0 (R) 22101.1 (H)	-14063.7 (R) -48053.3 (H)
	323.1 / 50.0	3.08	0.33	6.21	0.42	2.1635	0.0398		
	333.1 / 60.0	3.50	0.42	7.05	0.54	2.8378	0.0685		
	343.1 / 70.0	5.60	0.57	11.23	0.73	2.5917	0.1055		

(R): Data for RDX
(H): Data for HMX

As observed from the activity coefficient data in Table 2, the solubility of HMX relative to RDX shows the greater deviation from ideal values. Such deviations can be attributed to the interaction and chemical nature of RDX and HMX and the solvent. The enthalpy of mixing, $\Delta H_{mix,1}$, is a measure of solute-solvent interaction, whereas the enthalpy of fusion is solvent independent. The plot of $ln(x_1)$ versus T^{-1} was used to calculate the enthalpy of dissolution of RDX and HMX by using its slope, $dln(x_1)/d(T^{-1})$; the results are listed in Table 2.

The heat of dissolution of RDX and HMX in the binary EA/water solvent is exothermic. Note that the presence of water (up to 20%) in EA slightly enhances the solubility of HMX. A considerable variation and a decrease in the enthalpy of dissolution occurred with an increase in the water concentration. Deviations from such behaviour are seen as negative enthalpies of mixing, which drive the solids towards miscibility. A larger $\Delta H_{mix,1}$ results in a larger solvent-solute interaction and can increase the probability of the inclusion of solvent inside the crystals [11, 12].

3.3 Separation of RDX-HMX mixtures

Separation experiments (Section 2.4) were performed and the products were filtered at 70.0 °C, 50.0 °C and 30.0 °C. The products were characterized using HPLC analysis. The results showed that the weights of the solid products were 22.6 g, 23.7 g and 25.2 g with HMX purities of 99.5%, 97.8% and 93.2%, respectively. As the separation temperature was decreased, the purity of the recovered HMX decreased. Modelling of RDX and HMX solubility behaviour makes it possible to select and regulate the most suitable temperature and solvent composition for adequate separation conditions with high yield and high HMX purity.

Figure 2 shows a typical chromatogram and DTA curves for the RDX/HMX mixture before and after purification by filtering the material at 70.0 °C. The RDX and HMX appeared to be well separated under the analytical conditions. The RDX content of the purified HMX was significantly lower. The purified HMX decomposed in a single-step exothermic reaction with a peak temperature of 278.5 °C, and the RDX/HMX mixture showed multi-step decomposition with a peak temperature of about 266.2 °C. This can be attributed to the decomposition of RDX at the lower temperature and HMX at the higher temperature. The solvent content of the liquid filtrate was distilled and removed in the presence of an excess of water and a second precipitate formed. The weight of the recovered dried solid was about 7.2 g and comprised 81.5% RDX and 18.5% HMX. Analysis of these results shows that 98.3% of the RDX impurity in the HMX was recovered in the first precipitate; however this depended on the filtration temperature.
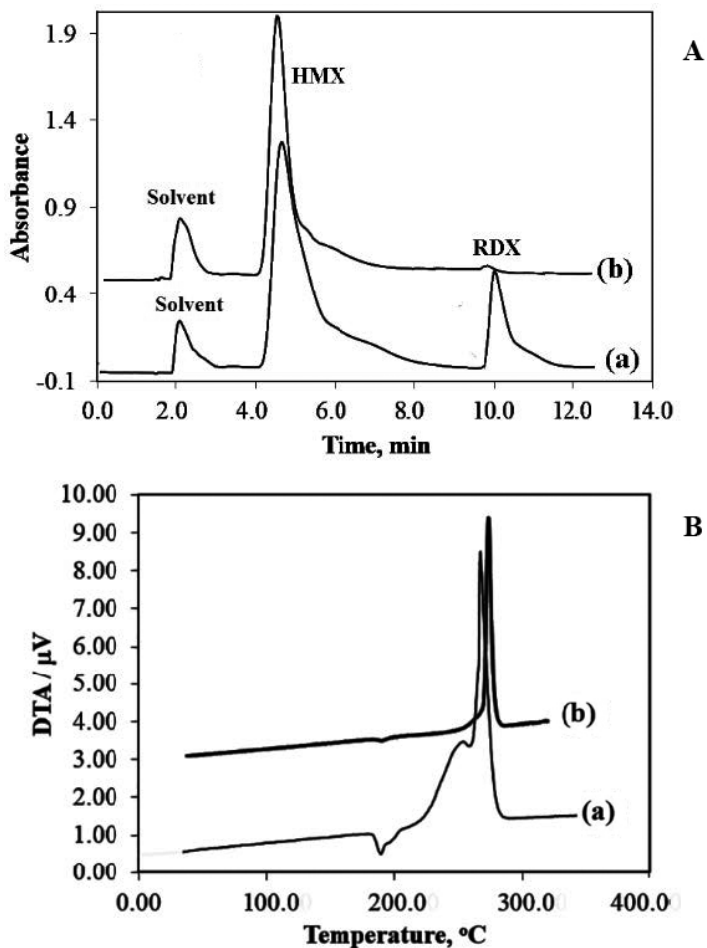
Figure 2. (A) HPLC chromatograms, and (B) DTA thermograms at a heating rate of 5 °C/min for (a) RDX-HMX mixture and (b) purified HMX from the separation conditions of 70.0 wt.% ethyl acetate/water and a temperature of 70.0 °C

4   Conclusions

The results showed that the solubility of RDX in EA is much higher than that of HMX and that the solubility of the explosives increased as the temperature is increased. The solubility of HMX also increased as the water content

was increased from 0.0% to 20.0% in the binary solvent, demonstrating the synergistic effect of EA and water on amplifying the solubility of this explosive. Considerable variation was observed along with an increase in the enthalpy of mixing with increased water content, which drives the solids towards miscibility. The results of simultaneous optimization led to the predicted conditions of a 70:30 EA/water mixture at 73.3 °C for a maximum response of 6.06 g RDX per 100 g of solvent and a minimum response of 0.48 g HMX per 100 g of solvent. Under these conditions, the solubility ratio of RDX to HMX was about 12.6-fold, representing very suitable separation conditions. The experimental results under the optimized conditions showed that decreasing the filtration temperature from 70 °C to 30 °C decreased the HMX purity from 99.5% to 93.2%. It is clear that decreasing the separation temperature decreased the purity of the solid HMX.

References

[1] Agrawal, J. P.; Hodgson, R. D. *Organic Chemistry of Explosives*. Wiley, **2007**; ISBN 978-0-470-02967-1.

[2] He, Zh.; Luo, J.; Lü, Ch.; Xu, R.; Li, J. Synthesis of HMX via Nitrolysis of DPT Catalyzed by Acidic Ionic Liquids. *Cent. Eur. J. Energ. Mater*. **2011**, *8*(2): 83-91.

[3] *HMX (Cyclotetramethylenetetranitramine)*. U.S. Army ARDEC, Military Standard, MIL-STD MIL-H-45444B, **1996**.

[4] Galante, E.; Haddad, A.; Marques, N. Application of Explosives in the Oil Industry. *Int*. *J. Oil Gas Coal Eng*. **2013**, *1*(2): 16-22.

[5] Dowson, R. E.; Mahaffey, D. M. *Process for the Separation of HMX from Mixtures Comprising RDX and HMX*. Patent US 3 676 425 A, **1972**.

[6] Boddu, V. M.; Damavarapu, R.; Abburi, K. *Adjusting Yield of a Manufacturing Process for Energetic Compound Through Solubility Modifications*. Patent US 8 002 917 B2, **2011**.

[7] Lee, B. M.; Lee, Y. W.; Kim, H. S.; Shim, J. S. *Method for Separation of HMX and HMX*. Patent US 8 759 514 B2, **2014**.

[8] Damiri, S.; Pouretedal, H. R.; Rahimi Assjerdi, A. Response Surface Optimization of the Purification Process of Cyclotrimethylenetrinitramine Explosive via Digestion in Binary Solvent Mixtures of Acetone/Water. *Separ. Sci. Technol*. Accepted. Author Manuscript. http://dx.doi.org/10.1080/01496395.2016.1251464.

[9] Wang, J.; Meng, Z. H.; Xue, M.; Qiu, L. L.; Zhang, C. F. Separation of 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane and 1,3,5-Trinitro-1,3,5-triazacyclohexane by Molecularly Imprinted Solid-Phase Extraction. *J. Sep. Sci*. Accepted. Author Manuscript. doi:10.1002/jssc.201601024.

[10] Sitzmann, M. E.; Foti, S. C. Solubilities of Explosives - Dimethylformamide as General Solvent for Explosives. *J. Chem. Eng. Data* **1975**, *20*: 53-55.

[11] Kim, K. J.; Kim, H. S.; Sim, J. S. Solubilities of Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine in γ-Butyrolactone + Water, Dimethylsulfoxide + Water, and *N*-Methyl pyrrolidone + Water. *J. Chem. Eng. Data* **2013**, *58*: 2410-2413.

[12] Kim, D. Y.; Kim, K. J. Solubility of Cyclotrimethylenetrinitramine (RDX) in Binary Solvent Mixtures. *J. Chem. Eng. Data* **2007**, *52*: 1946-1949.

[13] Svensson, L.; Nyqvist, J. O.; Westling, L. Crystallization of HMX from γ-Butyrolactone. *J. Hazard. Mater*. **1986**, *13*: 103-108.

[14] Basu, S.; Gawande, N. M.; Apte, M. E.; Narasimhan, V. L. Crystallization of HMX in Acetone/Water System. *Indian J. Chem. Techn*. **2004**, *11*: 575-581.

[15] Kröber, H.; Teipel, U. Crystallization of Insensitive HMX. *Propellants Explos. Pyrotech*. **2008**, *33*(1): 33-36.

[16] Ash, M.; Ash, I. *Handbook of Solvents*. 2nd ed., Synapse Information Resources, Inc. **2003**; ISBN 978-1-934764-48-0.

[17] MINITAB® Release 16 Statistical Software for Windows, **2010**, Minitab Inc., USA.

[18] Brereton, R. G. *Chemometrics: Data Analysis for the Laboratory and Chemical Plant*. Wiley, **2003**; ISBN 978-0-471-48978-8.