AD

AD-E404 042

Technical Report ARMET-TR-17053

SOLUBILITY REPORT OF LLM-172 [3,4-Bis (4-nitro-1,2,5-oxadiazole-3-yl)-1,2,5-Oxadiazole]

Kelley Caflin

July 2018

U.S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER

Munitions Engineering Technology Center

Picatinny Arsenal, New Jersey

The views, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

The citation in this report of the names of commercial firms or commercially available products or services does not constitute official endorsement by or approval of the U.S. Government.

Destroy by any means possible to prevent disclosure of contents or reconstruction of the document. Do not return to the originator.

REPORT DOCUMENTATION PAGE			*Form Approved OMB No. 0704-01-0188*

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (*From - To)*
July 2018	Final Report	January 2016 through January 2017

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
SOLUBILITY REPORT OF LLM-172 [3,4-Bis (4-nitro-1,2,5-oxadiazole-3-yl)-1,2,5-Oxadiazole]	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHORS	5d. PROJECT NUMBER
Kelley Caflin	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
U.S. Army ARDEC, METC Energetics, Warheads & Manufacturing Technology Directorate (RDAR-MEE-W) Picatinny Arsenal, NJ 07806-5000	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
U.S. Army ARDEC, ESIC Knowledge & Process Management (RDAR-EIK) Picatinny Arsenal, NJ 07806-5000	11. SPONSOR/MONITOR'S REPORT NUMBER(S) Technical Report ARMET-TR-17053

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The solubilities of LLM-172 [3,4-Bis (4-nitro-1,2,5-oxadiazole-3-yl)-1,2,5-Oxadiazole] in seven organic solvents were studied using the Avantium Crystal16™ parallel crystallizer. Solubility curves were constructed by monitoring the clear point of increasingly concentrated solute/solvent mixtures over a range in temperature. The solubility curves constructed were primarily exponential in nature; however, acetone exhibited a linear relationship. The van't Hoff plots were also constructed from the solubility data.

15. SUBJECT TERMS
Solubility LLM-172

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Kelley Caflin
U	U	U	SAR	19	19b. TELEPHONE NUMBER (Include area code) (973) 724-2657

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

CONTENTS

FIGURES

ACKNOWLEDGMENTS

Dr. Reddy Damavarapu is to be thanked for providing materials for testing. Thanks to Future Requirements for Enhanced Energetics for Decisive Munitions (FREEDM) for funding these efforts.

INTRODUCTION

The solubility of materials in other materials is a function of the interactions between the solute and the solvent. It is common to hear the phrase among chemists “like dissolves like.” Materials with polar groups tend to be more soluble in polar solvents, such as water, while non-polar substances tend to dissolve in materials like hydrocarbons. Interactions between solute-solvent molecules may include hydrogen bonding or dipole-dipole interactions (for polar materials) and van der Waals interactions (for non-polar). Temperature is also known to affect the solubility of materials. In general, the solubility of a solid material in liquid increases with the increase of temperature.

In this study, several solubility experiments were carried out for LLM-172 [3,4-Bis (4-nitro-1,2,5-oxadiazole-3-yl)-1,2,5-Oxadiazole]. Its chemical structure can be seen in figure 1. The LLM-172 solubility in various organic solvents were determined. Resulting solubility data can be used for recrystallization and formulation purposes.

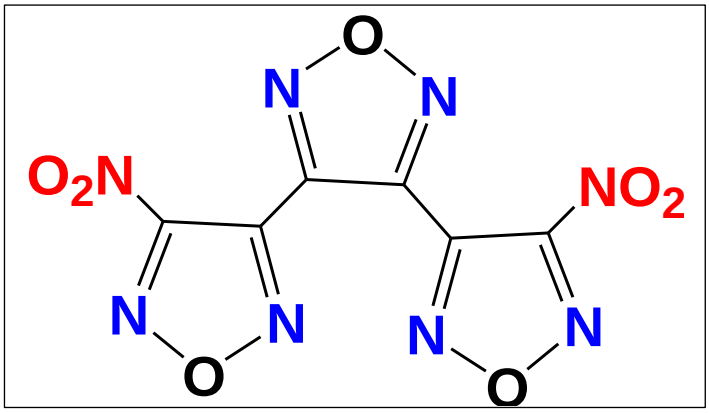

Figure 1
LLM-172

EXPERIMENTAL SECTION

Materials

The LLM-172 was synthesized at the U.S. Army Armament Research, Development and Engineering Center, Picatinny Arsenal, NJ, and determined pure by both nuclear magnetic resonance and melting point. Solvents used for solubility experiments were purchased from commercial sources and used without further purification. Reagent grade acetone was purchased from Pharmco-AAPER, Brookfield, CT. Ethyl Acetate (99.99% extra dry AcroSeal from Acros Organics, Belguim) was purchased from Fisher Scientific, Pittsburgh, PA. Methyl ethyl ketone, butyl acetate, 1-butanol, isopropanol and ethanol (200 proof) were purchased from Sigma Aldrich, St. Louis, MO.

Solubility Measurements

Solubility determinations of the pure components were determined on an Avantium Crystal16™, and were analyzed using the CrystalClear software package. Solvents investigated were acetone, ethyl acetate, ethanol, isopropanol, methyl ethyl ketone, butyl acetate, and n-butanol. In each experiment, the solute was weighed into a small, clear, and colorless high

performance liquid chromatography type vial equipped with a magnetic stir bar. Solvent was added and exact concentration recorded. The vials were placed into the Avantium Crystal16™, and temperature was cycled three times from 20 to approximately 5°C below the boiling point of solvent with 60-min. equilibration periods between heating and cooling. Ramp rates were 0.5 and -0.3°C/min.

The solubility of each vial solution was determined by identifying clear point temperatures, defined as the temperature at which the turbidity of the solution decreases upon heating and the solution becomes transparent. Graphing the clear point temperatures versus the concentration of the solution yields a solubility curve and associated equation.

RESULTS AND DISCUSSION

To interpret the data as an ideal system, a van't Hoff plot was calculated from each solubility curve shown in equation 1

$$\ln x = -\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (1)$$

in which x is the solute mole fraction, ΔH is the dissolution enthalpy, T0 (K) is a set-point temperature, and T (K) is the saturation temperature of the mole fraction x (ref. 1). As shown in figures 2 through 8 solubilities of LLM-172 in acetone, ethyl acetate, ethanol, isopropanol, methyl ethyl ketone, butyl acetate, and n-butanol.

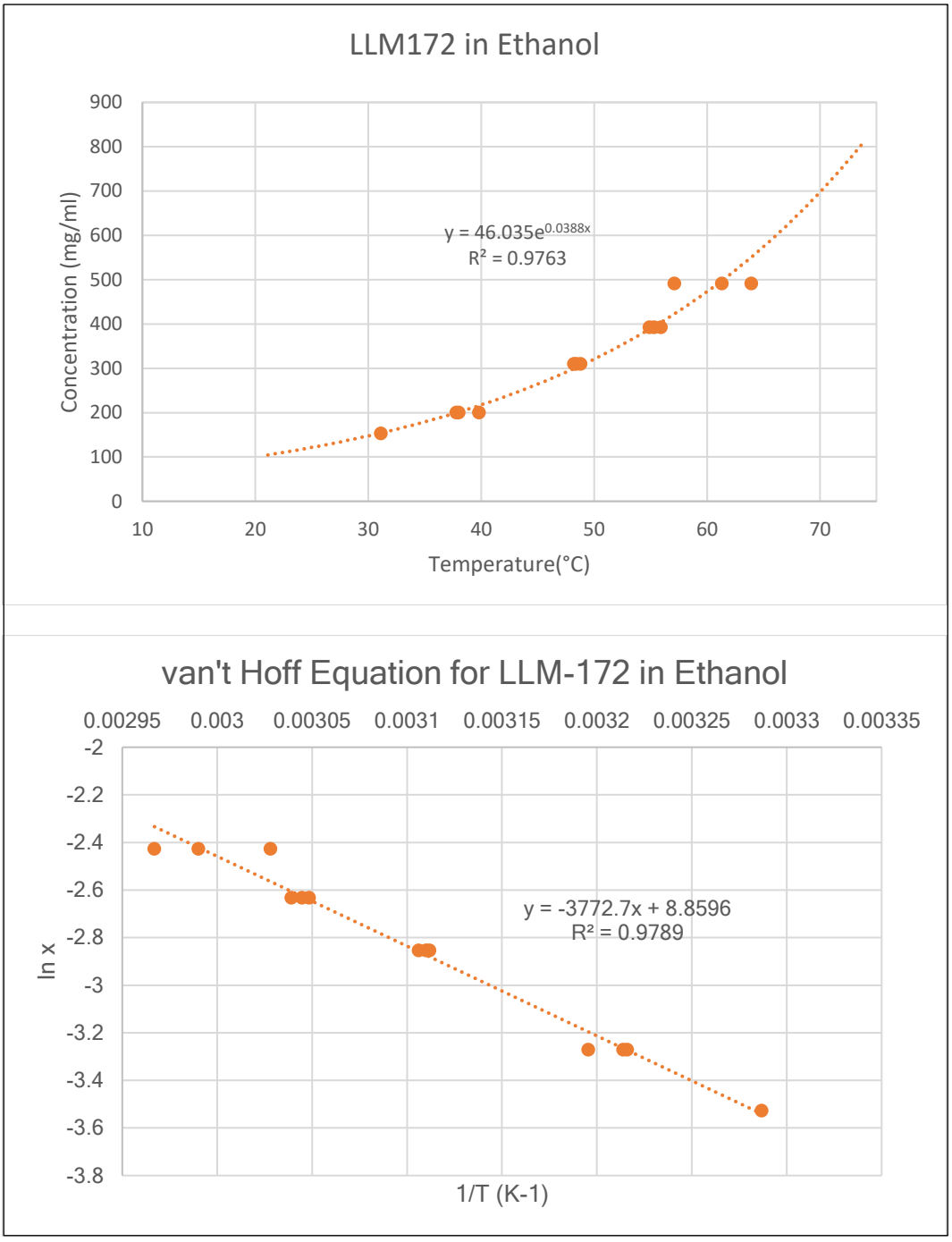

Figure 2
LLM-172 solubility curves in ethanol

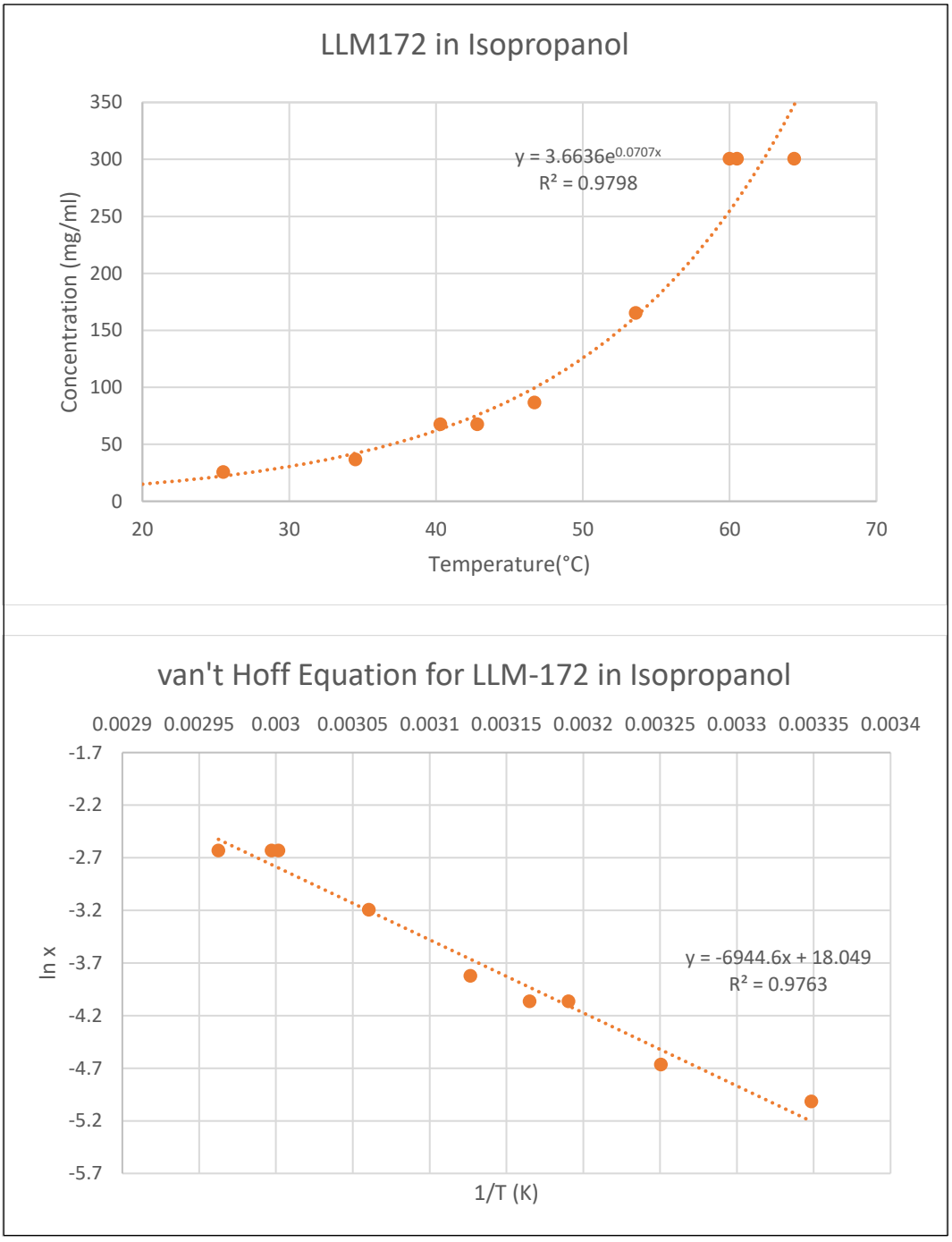

Figure 3
LLM-172 solubility curves in isopropanol

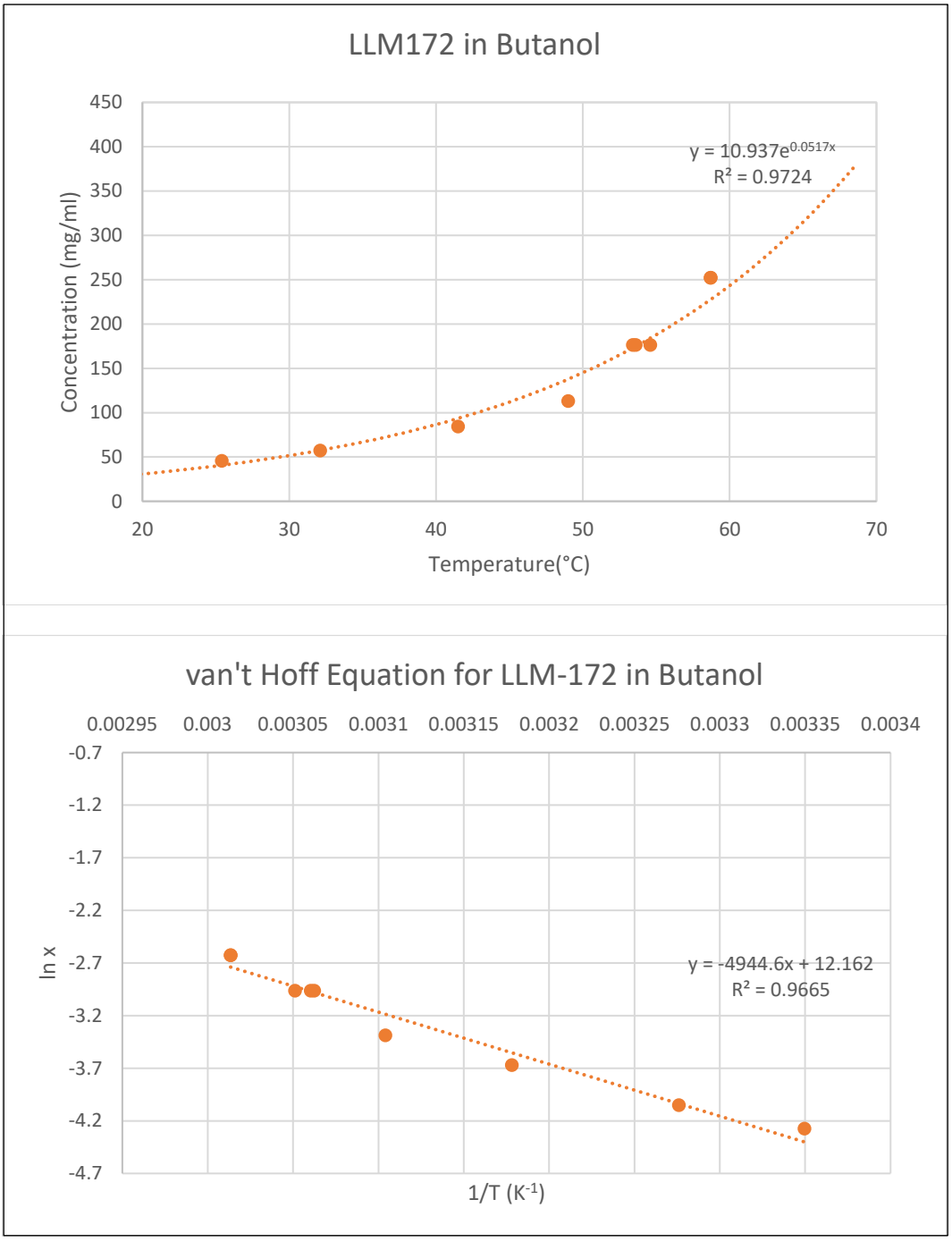

Figure 4
LLM-172 solubility curves in butanol

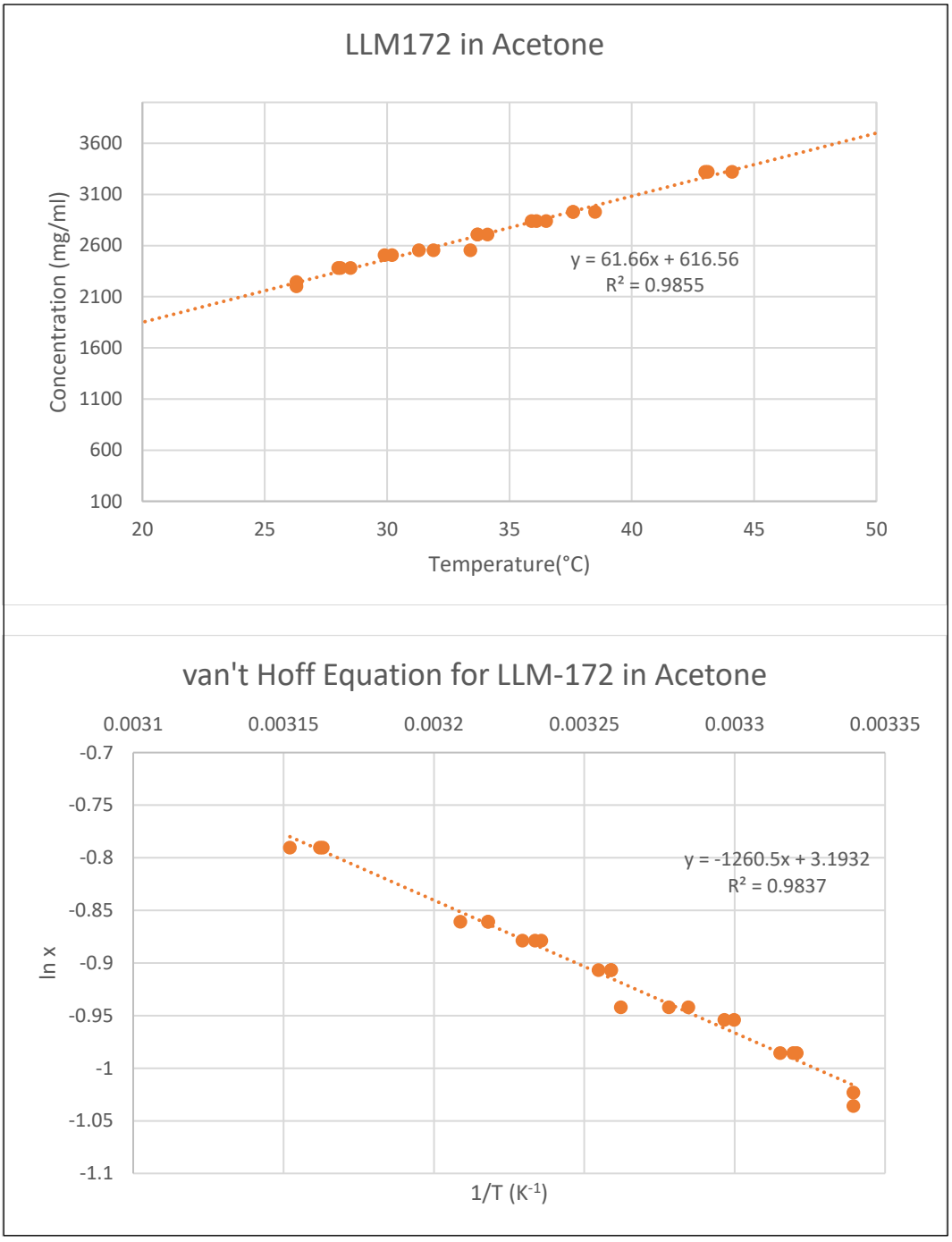

Figure 5
LLM-172 solubility curves in acetone

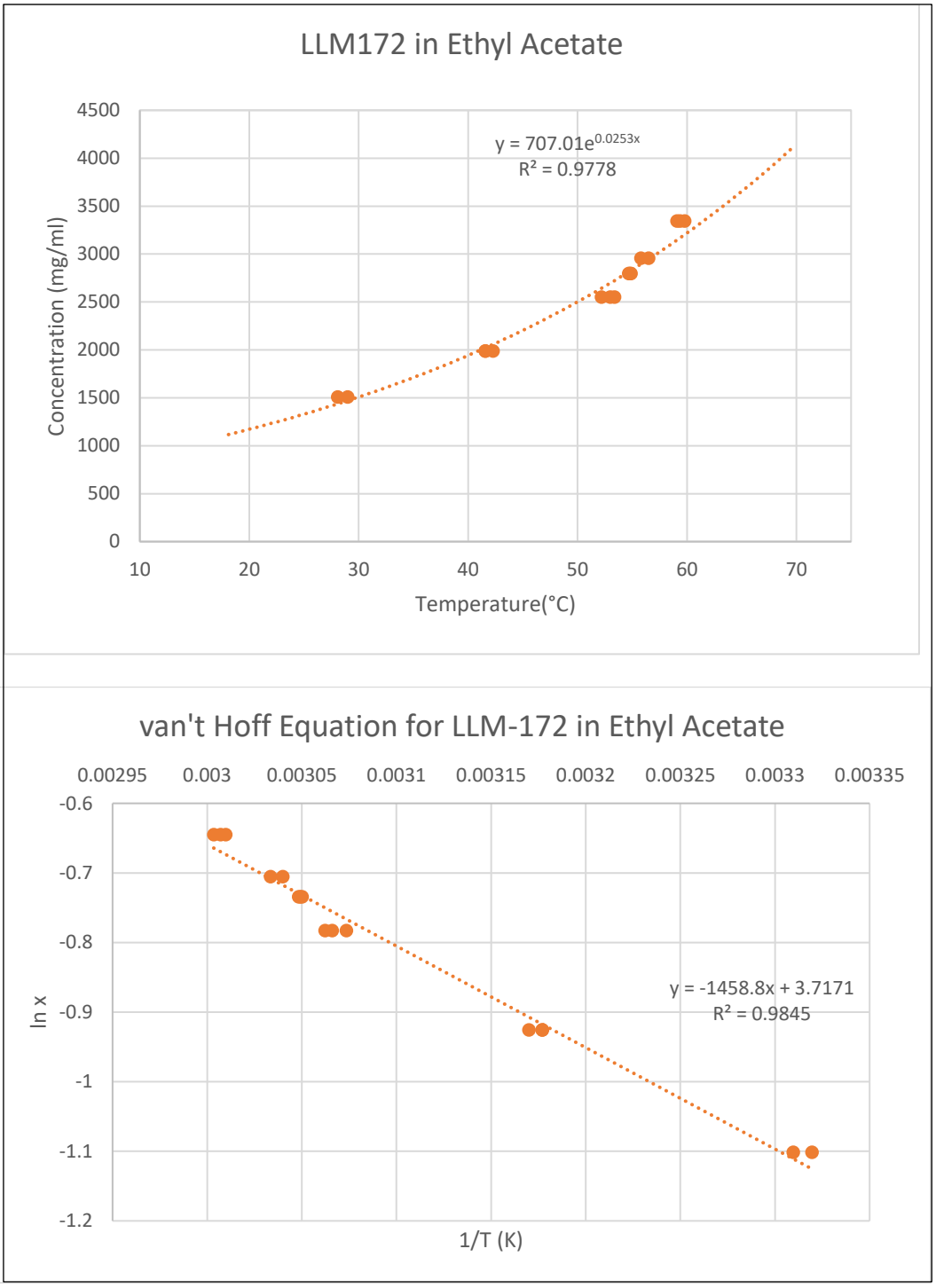

Figure 6
LLM-172 solubility curves in ethyl acetate

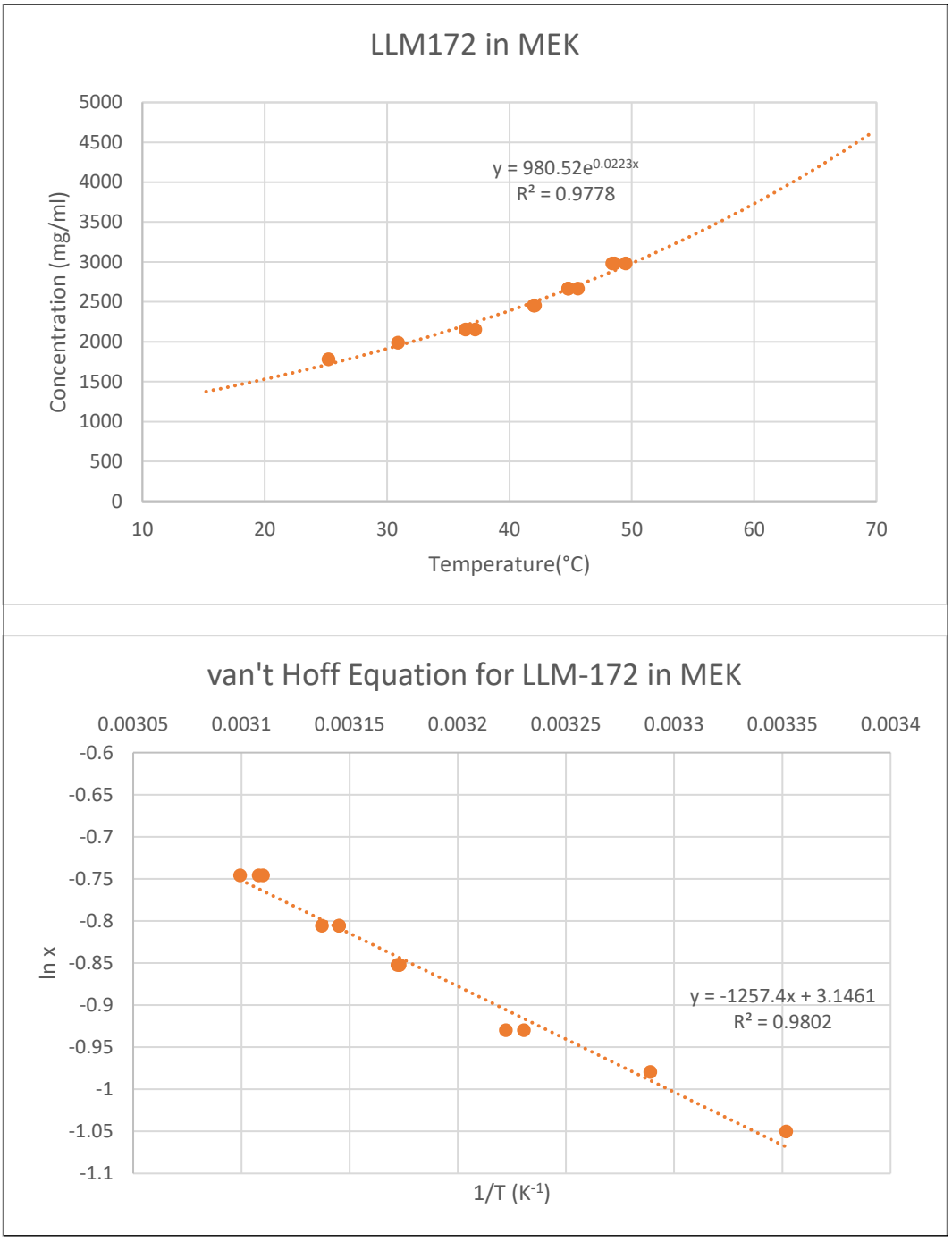

Figure 7
LLM-172 solubility curves in methyl ethyl ketone (MEK)

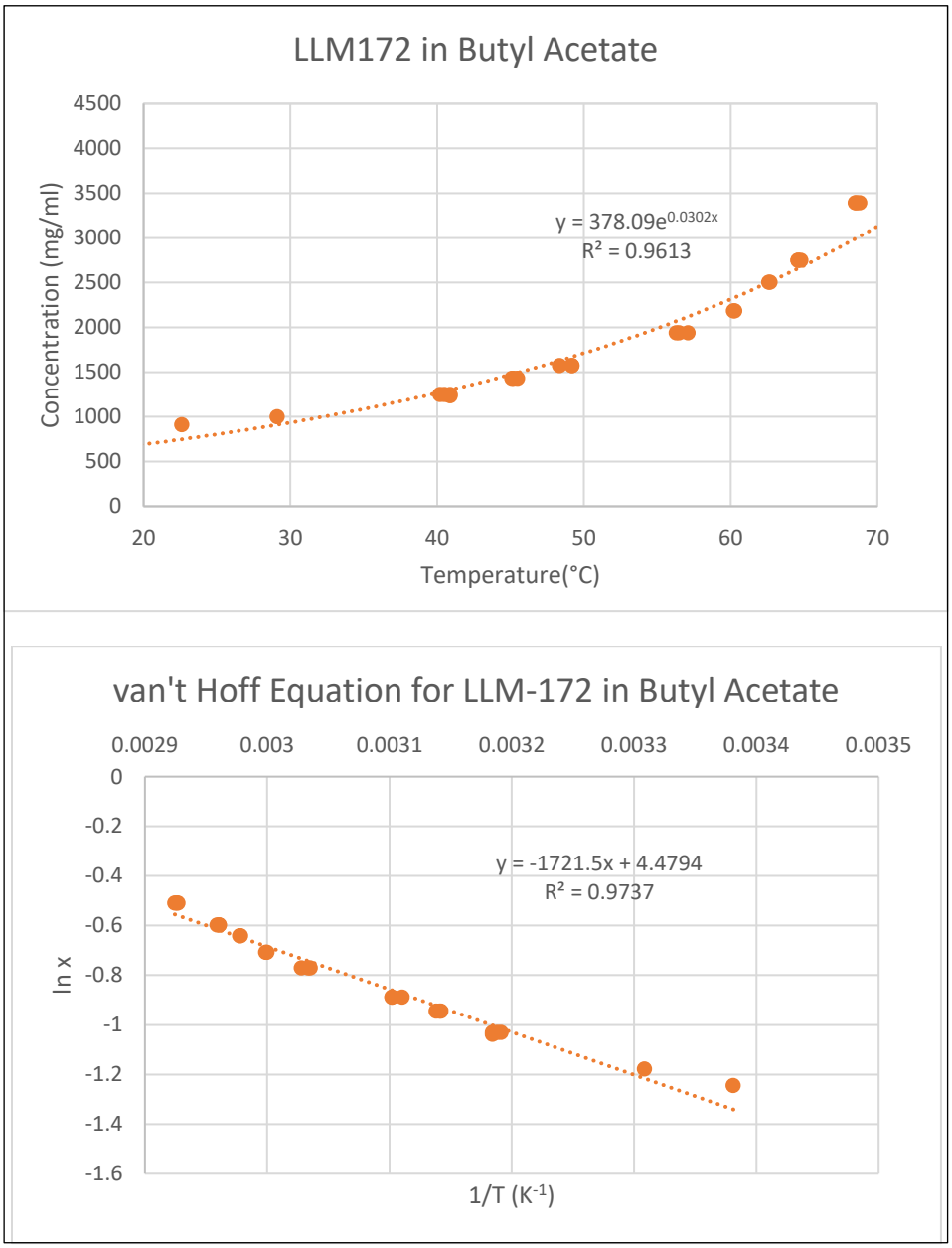

Figure 8
LLM-172 solubility curves in butyl acetate

CONCLUSIONS

Solubility curves and van't Hoff plots of LLM-172 [3,4-Bis (4-nitro-1,2,5-oxadiazole-3-yl)-1,2,5-Oxadiazole] were constructed for seven organic solvents LLM-172 using the Avantium Crystal16™ parallel crystallizer. The solubility curves constructed were primarily exponential in nature, however, acetone exhibited a linear relationship. The resulting regression lines show limited variation with all R^2 values greater than 0.96. The solubility curves or van't Hoff plots can be used to predict solubility, a temperature of interest.

REFERENCES

1. ter Horst, J.H., Deij, M.A., and Cains, P.W., “Discovering New Co-Crystals,” Crystal Growth & Design, Vol. 9, No. 3, pp. 1531-1537, 2009.

DISTRIBUTION LIST

U.S. Army ARDEC
ATTN: RDAR-EIK
RDAR-MEE-W, K.C. Caflin
Picatinny Arsenal, NJ 07806-5000

Defense Technical Information Center (DTIC)
ATTN: Accessions Division
8725 John J. Kingman Road, Ste. 0944
Fort Belvoir, VA 22060-6218

GIDEP Operations Center
P.O. Box 8000
Corona, CA 91718-8000
gidep@gidep.org

REVIEW AND APPROVAL OF ARDEC REPORTS

THIS IS A:

☒ **TECHNICAL REPORT** ☐ **SPECIAL REPORT**

☐ **MEMORANDUM REPORT** ☐ **ARMAMENT GRADUATE SCHOOL REPORT**

FUNDING SOURCE FREEDM Program FY16
[e.g., TEX3; 6.1 (ILIR, FTAS); 6.2; 6.3; PM funded EMD; PM funded Production/ESIP; Other (please identify)]

Solubility Report of LLM-172 ((3,4-Bis (4-nitro-1,2,5-oxadiazole-3-yl)-1,2,5-Oxadiazole)
Title

FREEDM Exploisves
Project

Kelley Caflin
Author/Project Engineer

Report number/Date received (to be completed by LCSD)

x2657 B3028
Extension Building

Room 14
Author's Office Symbol

PART 1. **Must be signed before the report can be edited.**

a. The draft copy of this report has been reviewed for technical accuracy and is approved for editing.

b. Use Distribution Statement A X, B___, C___, D___, E___, or F___ for the reason checked on the continuation of this form. Reason: _____

1. If Statement A is selected, the report will be released to the National Technical Information Service (NTIS) for sale to the general public. Only unclassified reports whose distribution is not limited or controlled in any way are released to NTIS.

2. If Statement B, C, D, E, or F is selected, the report will be released to the Defense Technical Information Center (DTIC) which will limit distribution according to the conditions indicated in the statement.

c. The distribution list for this report has been reviewed for accuracy and completeness.

Steven Nicolich 4/10/17
Division Chief (Date)

PART 2. To be signed either when draft report is submitted or after review of reproduction copy.

This report is approved for publication.

Scott Faluotico 29 Jun 2017
Division Chief (Date)