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Technical Report ARMET-TR-17067

**SOLUBILITY REPORT OF LLM-200 (BIS [3,3' (3-NITROFURAZANYL)] 5,5'-
1,2,5-OXADIAZOLE)**

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September 2018



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

Munitions Engineering Technology Center

Picatinny Arsenal, New Jersey

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-01-0188	
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1. REPORT DATE (DD-MM-YYYY) September 2018		2. REPORT TYPE Final		3. DATES COVERED (From - To) February 2017 to June 2017
4. TITLE AND SUBTITLE SOLUBILITY REPORT OF LLM-200 (BIS [3,3' (3-NITROFURAZANYL)] 5,5'-1,2,5-OXADIAZOLE)			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHORS Dr. Kelley Cafilin			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army ARDEC, METC Energetics & Warheads Directorate (RDAR-MEE-W) Picatinny Arsenal, NJ 07806-5000			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army ARDEC, ESIC Knowledge Management Office (RDAR-EIK) Picatinny Arsenal, NJ 07806-5000			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) Technical Report ARMET-TR-17067	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT Solubilities of LLM-200 in six 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. The LLM-200 was very slightly soluble in methylene chloride but not soluble in water. The van't Hoff plots were also constructed from the solubility data.				
15. SUBJECT TERMS LLM-200 Solubility				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 17
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U		
			19b. TELEPHONE NUMBER (Include area code) (973) 724-2657	

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ACKNOWLEDGMENTS

Dr. Reddy Damavarapu is to be thanked for providing materials for testing. Thanks to Energetics Qualification Testing for funding these efforts.

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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 amongst chemists "like dissolves like." Materials with polar groups tend to be more soluble in polar solvents, such as water, while nonpolar 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 nonpolar). 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-200. Its chemical structure can be seen in figure 1. The LLM-200 solubility in various organic solvents was determined. Resulting solubility data can be used for recrystallization and formulation purposes.

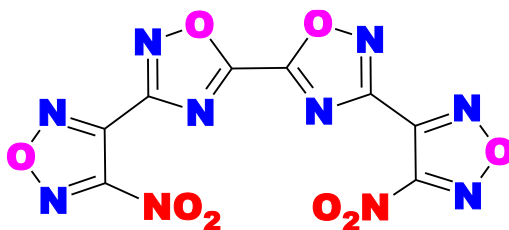


Figure 1
LLM-200 (Bis [3,3' (3-nitrofurazanyl)] 5,5'-1,2,5-Oxadiazole)

EXPERIMENTAL SECTION

Materials

The LLM-200 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, except water, used for solubility experiments were purchased from commercial sources and used without further purification. Reagent grade acetone was purchased from Sigma Aldrich Lot MKCB1302V. Ethyl Acetate (99.99% extra dry AcroSeal from Acros Organics, Belgium) was purchased from Fisher Scientific, Pittsburgh, PA. Methyl ethyl ketone (MEK) was purchased from Sigma Aldrich, St. Louis, MO. Methylene chloride was purchased from Sigma Aldrich Lot SHBF79144. Tetrahydrofuran (THF) was purchased from Sigma Aldrich Lot SHBD68374. High performance liquid chromatography (HPLC) grade water was produced using an in-house purification system.

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, MEK, methylene chloride, THF, and water. In each experiment, the solute was weighed into a small, clear, and colorless HPLC-type vial equipped with a magnetic stir bar. Solvent was added, and the exact concentration was recorded. The vials were placed into the Avantium Crystal16™, and the 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.

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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 using the equation below,

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

in which x is the solute mole fraction, ΔH is the dissolution enthalpy, T_0 (K) is a set-point temperature, and T (K) is the saturation temperature of the mole fraction x (ref. 1). The solubilities of LLM-172 in acetone, ethyl acetate, MEK, methylene chloride, THF, and water are shown in figures 2 through 5.

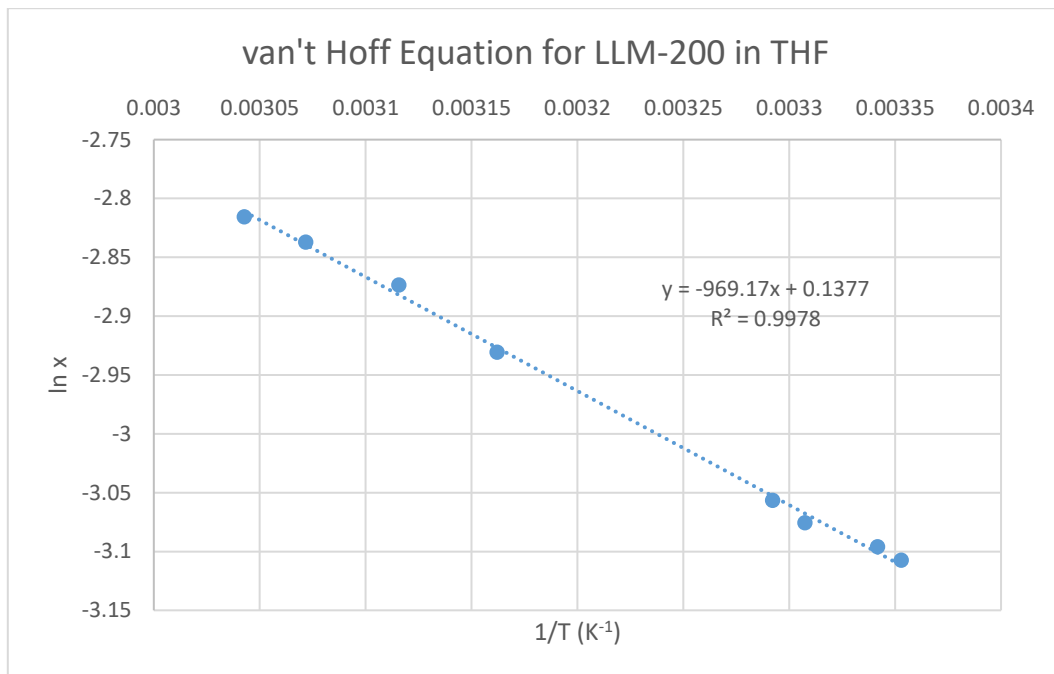
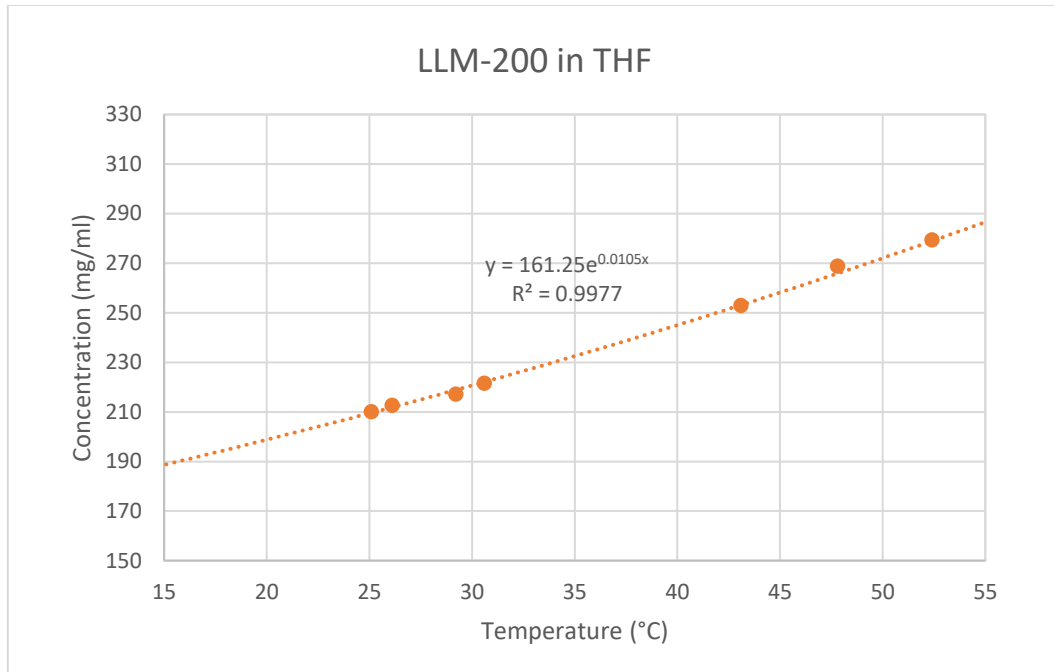


Figure 2
LLM-200 solubility curves in THF

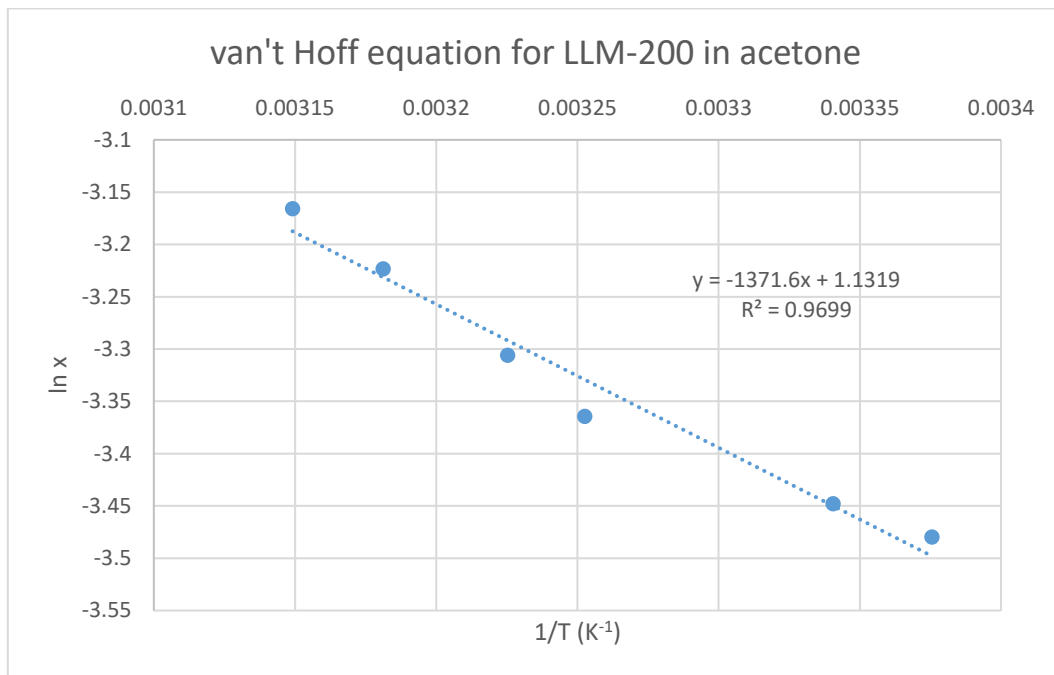
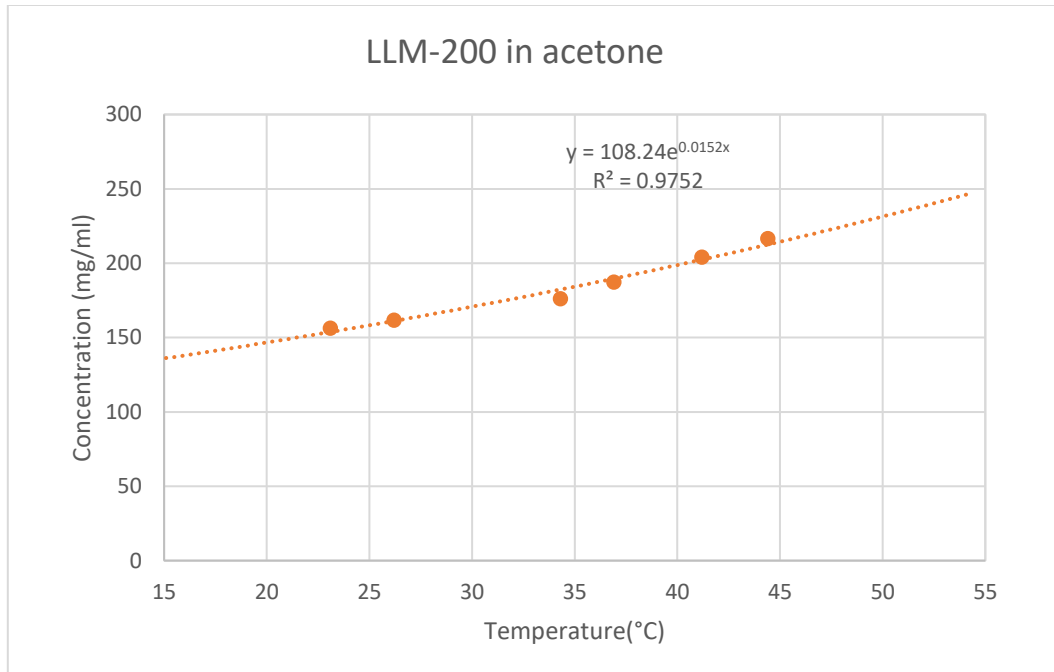


Figure 3
LLM-200 solubility curves in acetone

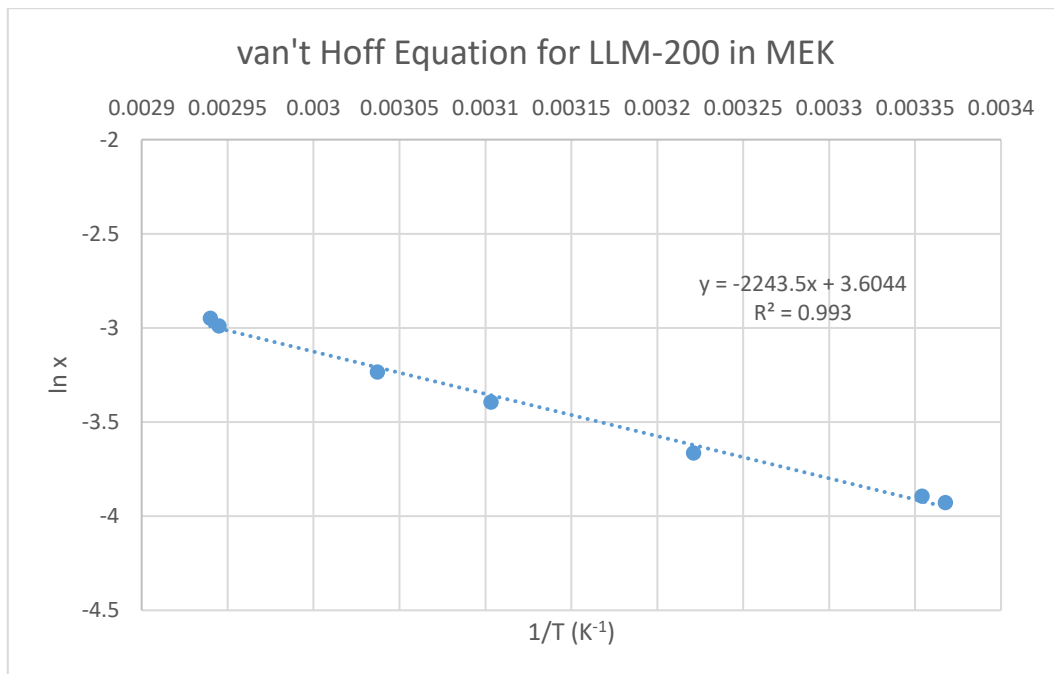
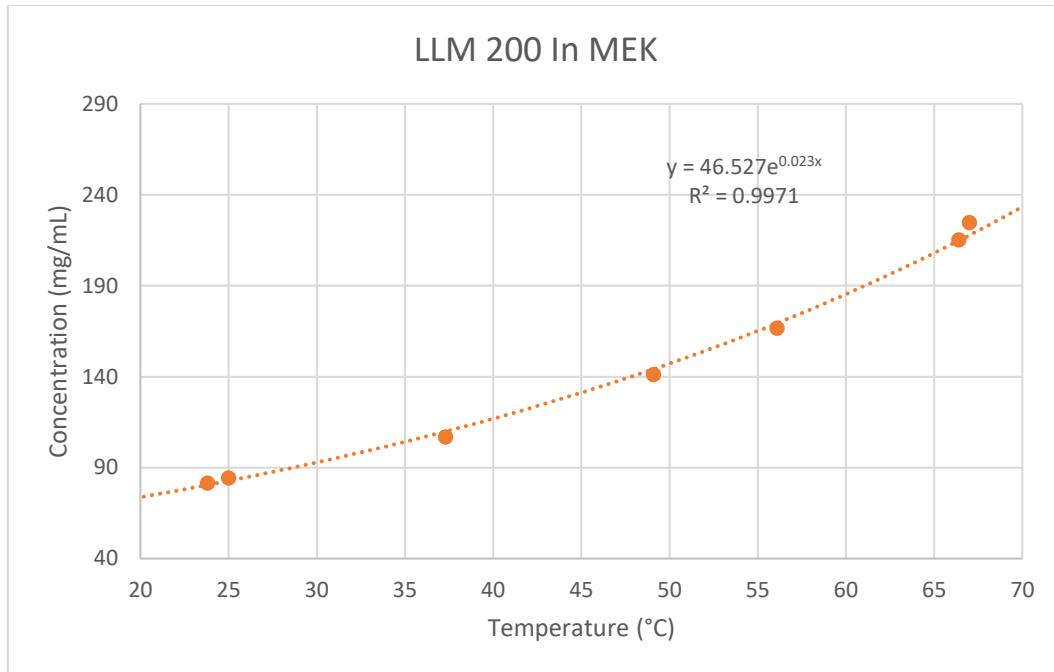


Figure 4
LLM-200 solubility curves in MEK

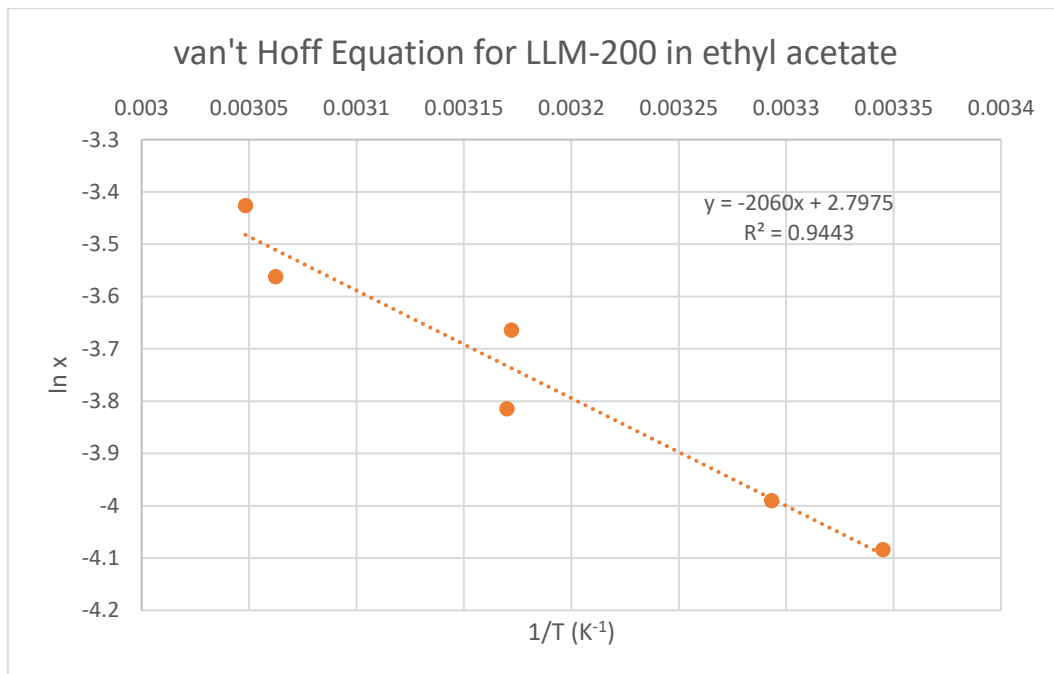
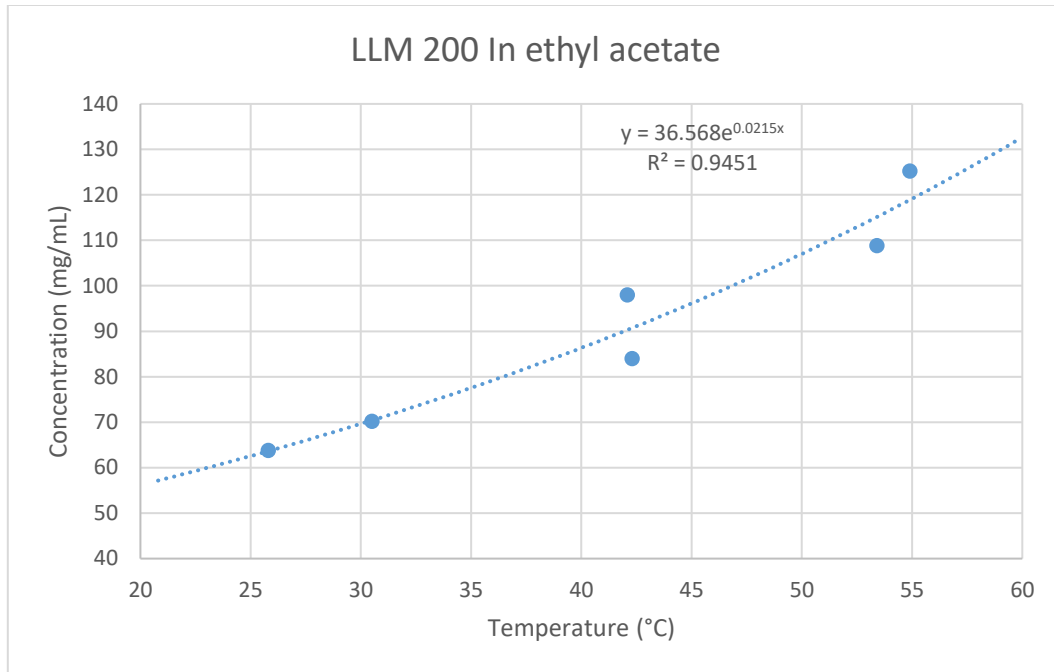


Figure 5
LLM-200 solubility curves in ethyl acetate

Methylene Chloride

Samples were constructed with concentrations as low as 0.5 mg/mL and heated to 35°C; clear points were obtained for samples ranging from 0.5 to 1.7 mg/mL. However, due to the limitations of the instrument, a direct trend could not be determined. In general, LLM-200 is very slightly soluble in methylene chloride, approximately 1.7 mg/mL at 28°C.

Water

Samples were constructed with concentrations as low as 2.2 mg/mL and heated to 90°C; a clear point was not obtained. The LLM-200 does not appear to be soluble in water.

CONCLUSIONS

Solubility curves and van't Hoff plots of LLM-172 were constructed for four organic solvents with LLM-200 using the Avantium Crystal16™ parallel crystallizer. The solubility curves constructed were exponential in nature. The resulting regression lines show limited variation with all R2 values greater than 0.94. The solubility curves or van't Hoff plots can be used to predict the solubility of LLM-200 at a temperature of interest. The LLM-200 showed very limited solubility in methylene chloride, but a trend line could not be obtained. The LLM-200 appears to be insoluble in water.

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[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-200

(Bis [3,3' (3-nitrofurazany)] 5,5'-1,2,5-Oxadiazole)

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