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Technical Report ARMET-TR-19022

**SOLUBILITY REPORT OF 3-(5-AMINO-1,2,4-OXADIAZOL-3-YL)-4-NITRO-
1,2,5-OXADIAZOLE (LLM 201)**

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September 2020



U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT
COMMAND ARMAMENTS CENTER

Munitions Engineering Technology Center

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1. REPORT DATE (DD-MM-YYYY) September 2020		2. REPORT TYPE Final		3. DATES COVERED (From - To) August 2018 to October 2018
4. TITLE AND SUBTITLE Solubility Report of 3-(5-amino-1,2,4-oxadiazol-3-yl)-4-nitro-1,2,5-oxadiazole (LLM 201)			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHORS Dr. Kelley C. Caflin			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army CCDC AC, METC Energetics and Warheads Directorate (FCDD-ACM-EW) Picatinny Arsenal, NJ 07806-5000			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army CCDC AC, ESIC Knowledge & Process Management Office (FCDD-ACE-K) Picatinny Arsenal, NJ 07806-5000			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) Technical Report ARMET-TR-19022	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.				
13. SUPPLEMENTARY NOTES				
14. ABSTRACT Solubilities of 3-(5-amino-1,2,4-oxadiazol-3-yl)-4-nitro-1,2,5-oxadiazole (LLM 201) in four common 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. van't Hoff plots were also constructed from the solubility data.				
15. SUBJECT TERMS Solubility LLM 201				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 15
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U		
			19b. TELEPHONE NUMBER (Include area code) (973) 724-2657	

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

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ACKNOWLEDGMENTS

The author would like to thank Dr. Reddy Damavarapu for providing materials for testing.

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 “like dissolves like” amongst chemists. 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 3-(5-amino-1,2,4-oxadiazol-3-yl)-4-nitro-1,2,5-oxadiazole (LLM 201). Its chemical structure can be seen in figure 1. LLM 201 solubility in various solvents was determined. Resulting solubility data can be used for synthesis, recrystallization, and formulation purposes.

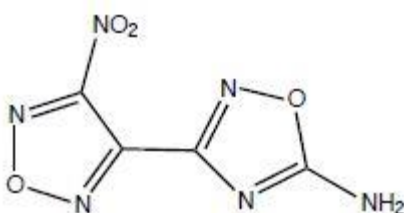


Figure 1
LLM 201 component structure

EXPERIMENTAL SECTION

Materials

LLM 201 was synthesized by Dr. Reddy Damavarapu and determined pure by nuclear magnetic resonance (NMR). 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, Belgium) was purchased from Fisher Scientific, Pittsburgh, PA. Ethanol (200 proof) was purchased from Sigma Aldrich, St. Louis, MO. High performance liquid chromatography (HPLC) grade water was produced on-site using a purification system.

Solubility Measurements

Solubility measurements of LLM 201 were acquired on an Avantium Crystal16™ and were analyzed using CrystalClear software. Solvents investigated were acetone, ethyl acetate, ethanol, and water. In each experiment, the solute was weighed into a small, clear, 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 temperature was cycled three times from 20 to approximately 5 °C below the boiling point of the 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

A van't Hoff plot was constructed from each solubility curve using 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, T_0 (K) is a reference temperature, and T (K) is the saturation temperature of the mole fraction x (ref. 1). The results of this equation are a linear relationship of $\ln x$ versus T^{-1} when the entropy and enthalpy are constant with temperature change. Using the resulting trend line, one can calculate the solubilities at other temperatures. Figures 2 through 9 show the solubility curves and van't Hoff equations for LLM 201 in acetone, ethyl acetate, ethanol, and water.

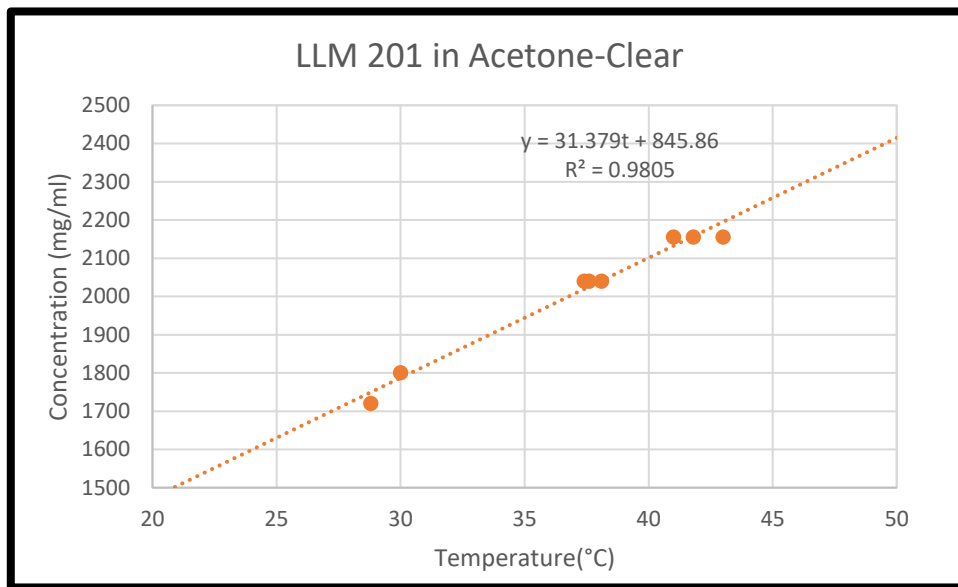


Figure 2
LLM 201 solubility curve in acetone

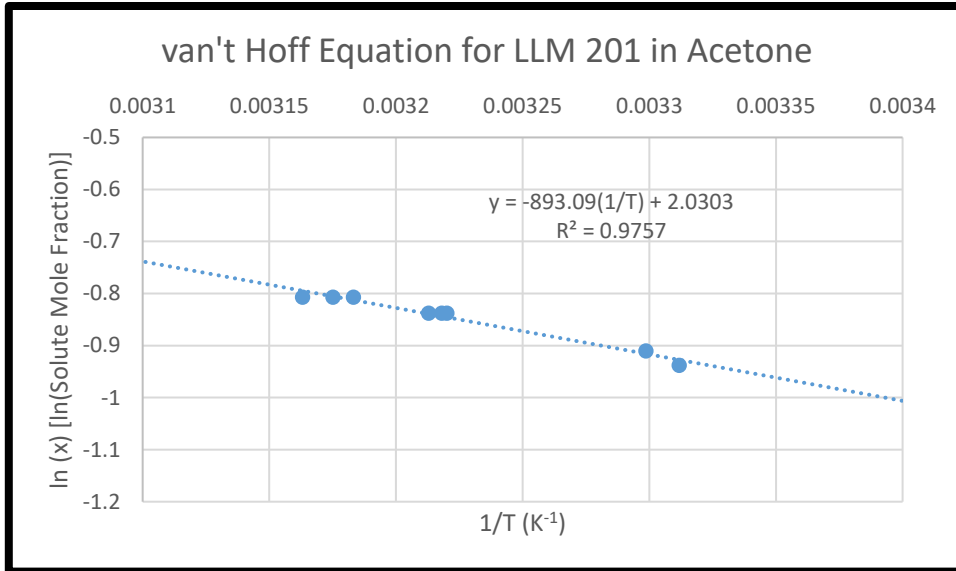


Figure 3
van't Hoff equation for LLM 201 in acetone

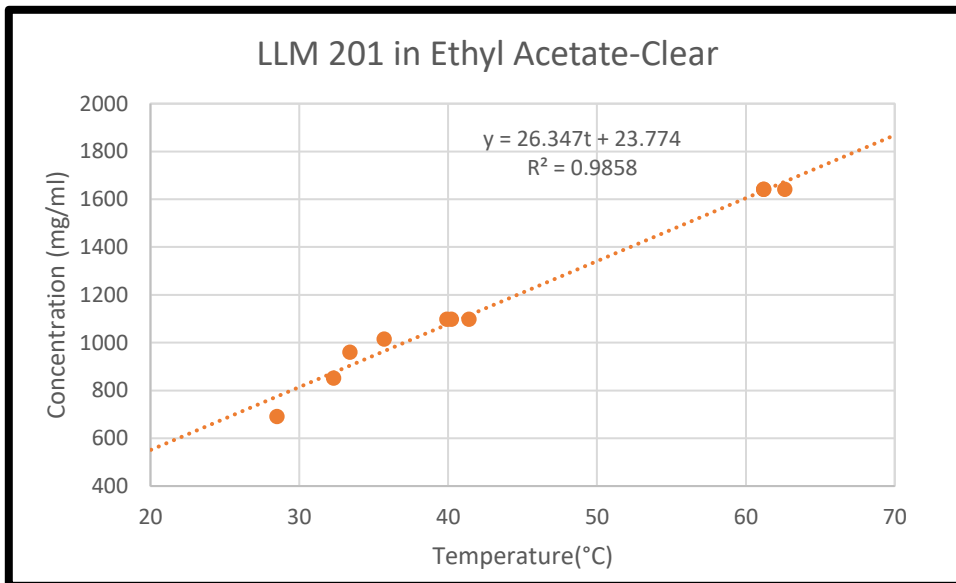


Figure 4
LLM 201 solubility curve in ethyl acetate

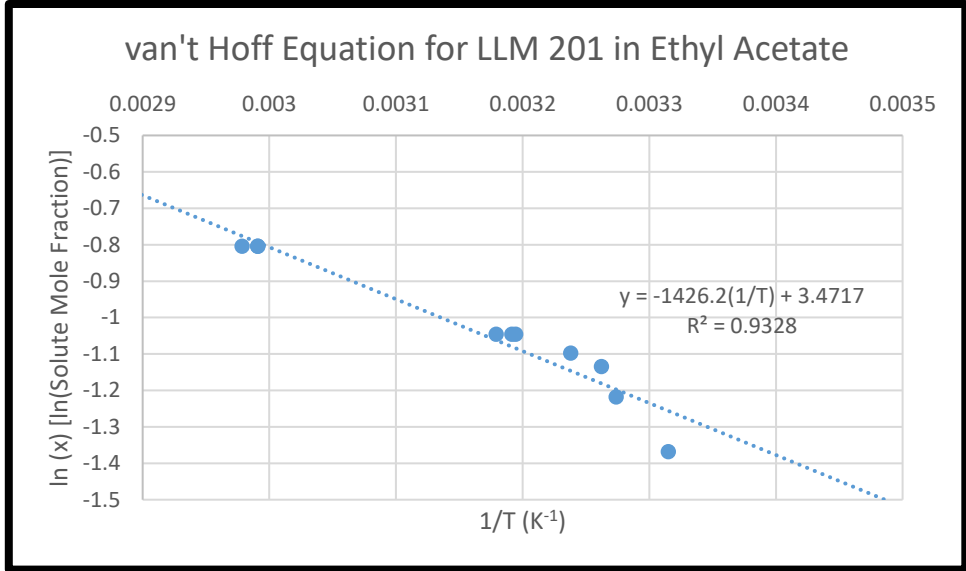


Figure 5
van't Hoff equation for LLM 201 in ethyl acetate

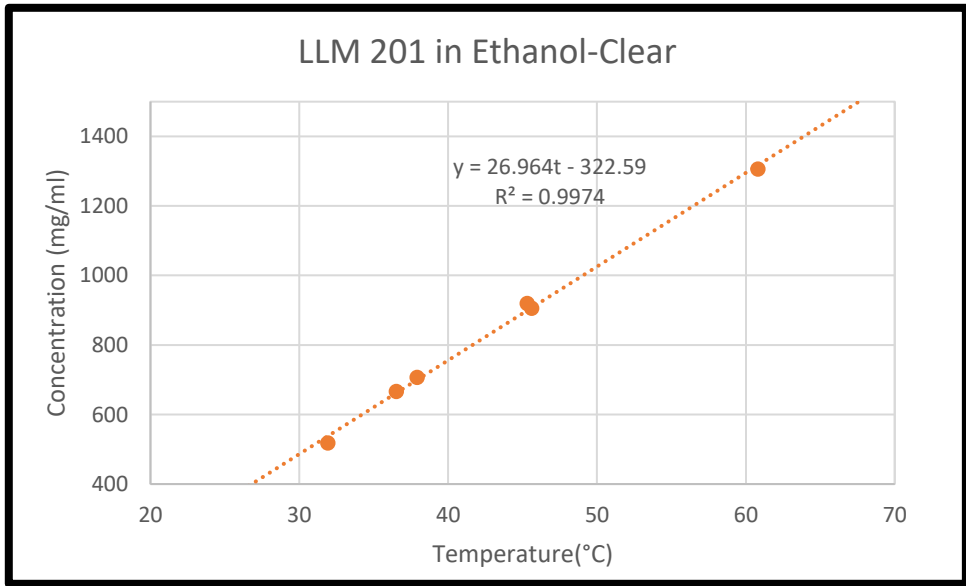


Figure 6
LLM 201 solubility curve in ethanol

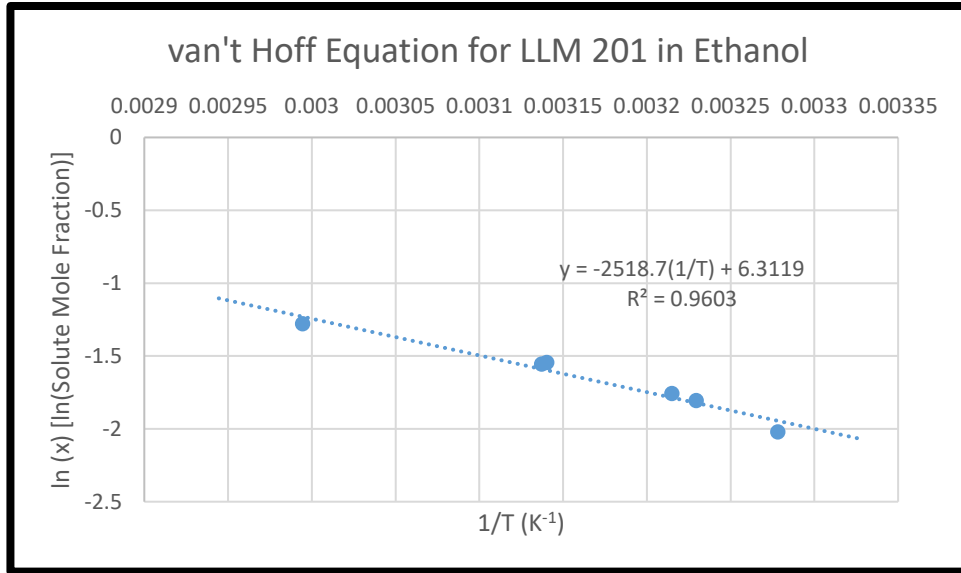


Figure 7
van't Hoff equation for LLM 201 in ethanol

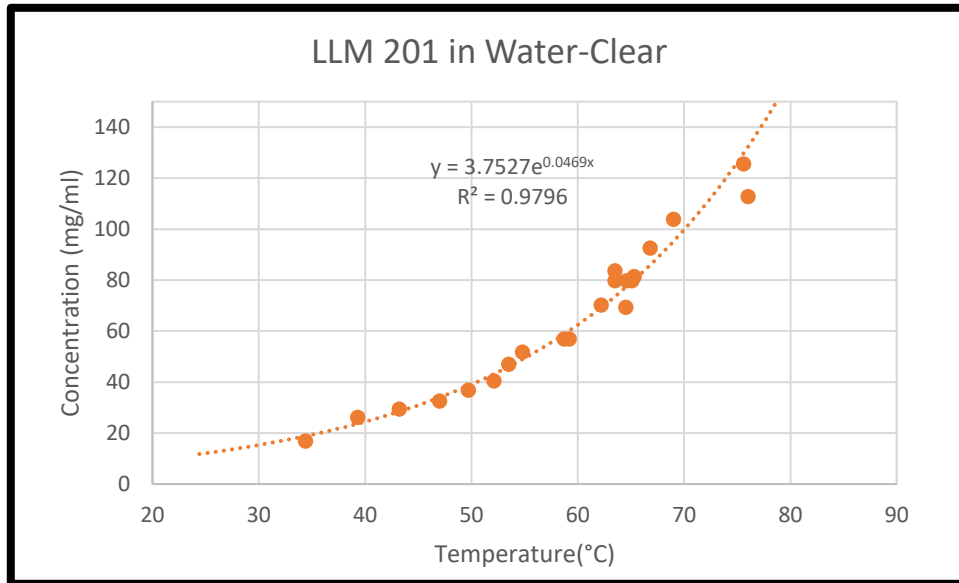


Figure 8
LLM 201 solubility curve in water

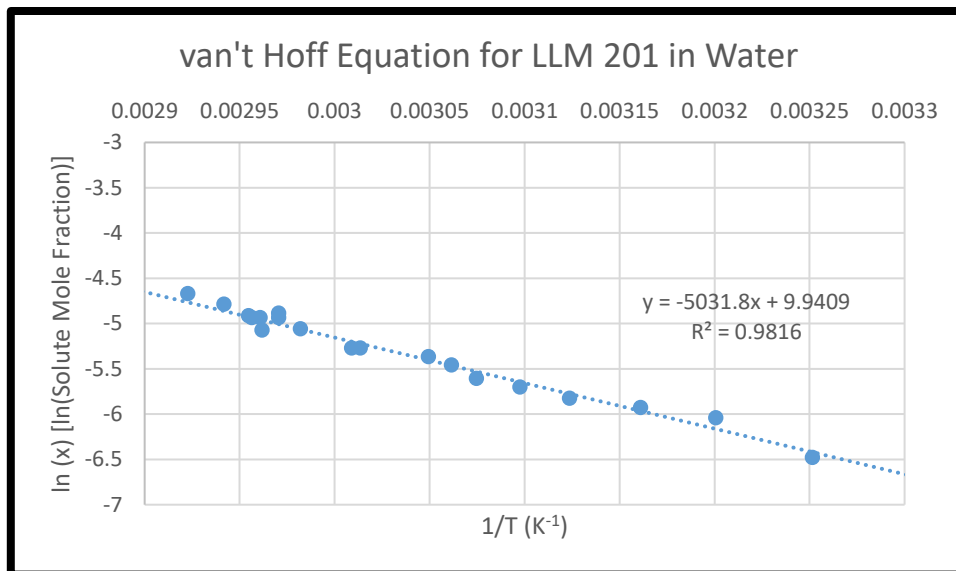


Figure 9
van't Hoff equation for LLM 201 in water

CONCLUSIONS

Solubility curves and van't Hoff plots of 3-(5-amino-1,2,4-oxadiazol-3-yl)-4-nitro-1,2,5-oxadiazole (LLM 201) were constructed for four solvents using the Avantium Crystal16™ parallel crystallizer. The solubility curves constructed were linear and exponential in nature. The resulting regression lines show limited variation with all R^2 values greater than 0.9328. The solubility curves or van't Hoff plots can be used to predict solubility at the temperature of interest.

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Solubility Report of 3-(5-amino-1,2,4-oxadiazol-3-yl)-4-nitro-1,2,5-oxadiazole (LLM 201)

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