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AD-E404 423

Technical Report ARMET-TR-20074

SOLUBILITY REPORT OF 2,4,6-TRINITROTOLUENE (TNT)

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December 2022

U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND ARMAMENTS CENTER

Munitions Engineering and Technology Center

Picatinny Arsenal, New Jersey

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REPORT DOCUMENTATION PAGE

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED START DATE	END DATE
December 2022	Final	April 2015	June 2019

4. TITLE AND SUBTITLE
Solubility Report of 2,4,6-Trinitrotoluene (TNT)

5a. CONTRACT NUMBER	5b. GRANT NUMBER	5c. PROGRAM ELEMENT NUMBER
5d. PROJECT NUMBER	**5e. TASK NUMBER**	**5f. WORK UNIT NUMBER**

6. AUTHOR(S)
Dr. Kelley Caflin

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
U.S. Army DEVCOM AC, METC Energetics and Warheads Directorate (FCDD-ACM-EW) Picatinny Arsenal, NJ 07806-5000	N\A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)	11. SPONSOR/MONITOR'S REPORT NUMBER(S)
U.S. Army DEVCOM AC, ESIC Knowledge & Process Management Office (FCDD-ACE-K) Picatinny Arsenal, NJ 07806-5000		Technical Report ARMET-TR-20074

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

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Solubilities of 2,4,6-trinitrotoluene (TNT) in five 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 2,4,6-trinitrotoluene TNT Crystal16 Crystallizer

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
U	U	U	SAR	17

19a. NAME OF RESPONSIBLE PERSON	19b. PHONE NUMBER (Include area code)
Kelley Caflin	(973) 724-2657

Standard Form 298 (REV. 5/2020)
Prescribed by ANSI Std. Z39.18

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ACKNOWLEDGMENTS

The author would like to thank Dr. Reddy Damavarapu and Philip Samuels for funding this research. The author would also like to thank Peggy Sanchez for her guidance with initial solubility measurements of TNT in ethanol and ethyl acetate.

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 temperature.

In this study, several solubility experiments were carried out for 2,4,6-trinitrotoluene (TNT). Its chemical structure can be seen in figure 1. The solubility of TNT in various solvents was determined. The resulting solubility data can be used for synthesis, recrystallization, and formulation purposes.

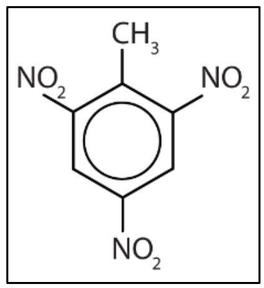


Figure 1
Chemical structure of TNT

EXPERIMENTAL SECTION

Materials

The TNT used for ethanol, chloroform, and cyclohexane was Flake TNT, NSN: 1376006283333, lot: CIB93B006-076. The specific lot of TNT for ethyl acetate and acetone was not recorded; however, it was stock Flake TNT. Flake TNT was crushed using a mortar and pestle to reduce sample size to ease filling of vials and stir bar mixing. Solvents used for solubility experiments were purchased from commercial sources and used without further purification. They are as follows: reagent grade acetone from Pharmco-AAPER, Brookfield, CT; ethyl acetate (99.99% extra dry AcroSeal from Acros Organics, Belgium) from Fisher Scientific, Pittsburgh, PA; ethanol: Sigma Aldrich 200 Proof Anhydrous ≥99.5%, lot: SHBJ3722; cyclohexane: Uvasol Cyclohexane, lot: I0927322 749; and chloroform: Uvasol Chloroform, lot: K50753747 842.

Solubility Measurements

Solubility measurements of TNT were acquired on an Avantium Crystal16™ and analyzed using CrystalClear software. Solvents investigated were acetone, ethyl acetate, ethanol, cyclohexane, and chloroform. 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. A solvent was added and the exact concentration of the solution was recorded. The vials were placed into the Avantium Crystal16™, and temperature was cycled three times from 20 °C 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.

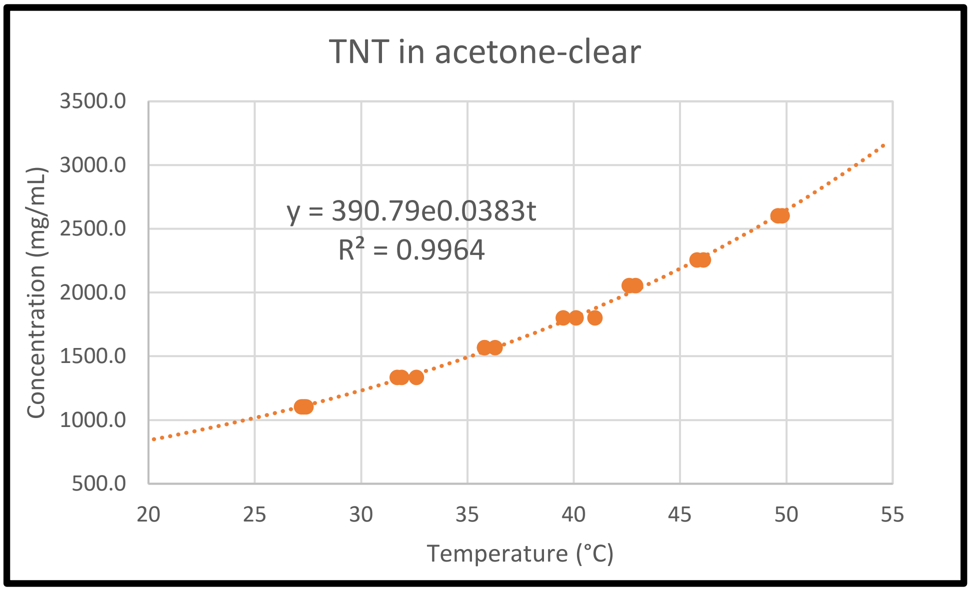
The solubility of each vial solution was determined by identifying clear point temperatures, which are defined as the temperature at which the turbidity of the solution decreases upon heating and the solution becomes transparent. Graphing the clear point temperatures versus the concentration of the solution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

RESULTS AND DISCUSSION

A van't Hoff plot was constructed from each solubility curve using the following equation:

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

where x is the solute mole fraction, ΔH is the dissolution enthalpy, R is the ideal gas constant, T_0 is a reference temperature (K), and T is the saturation temperature (K) of the mole fraction x (ref. 1). The results of this equation are a linear relationship of the natural logarithm of x (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. Shown in figures 2 through 6 are the solubility curves of TNT in acetone, ethyl acetate, ethanol, cyclohexane, and chloroform.



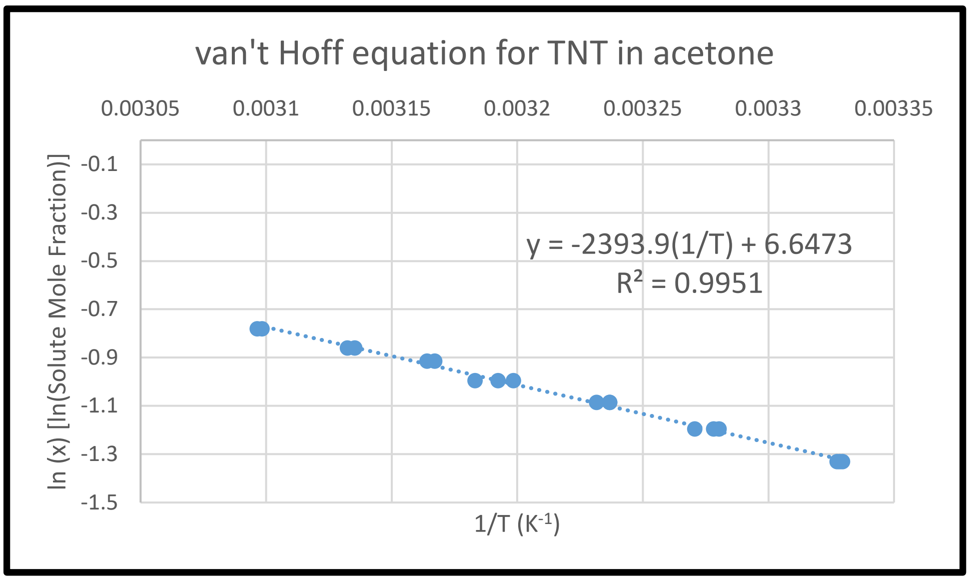


Figure 2
TNT solubility curves in acetone

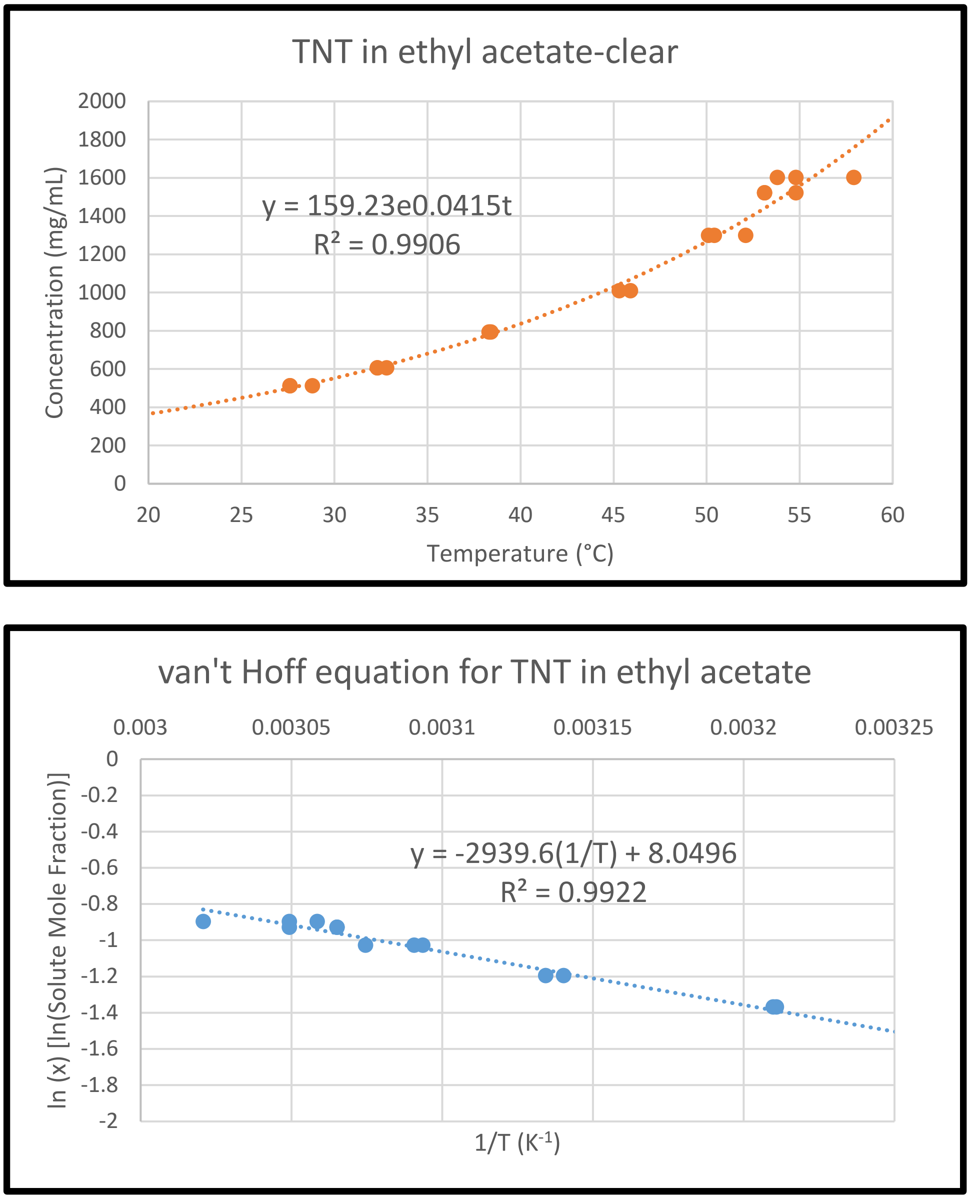
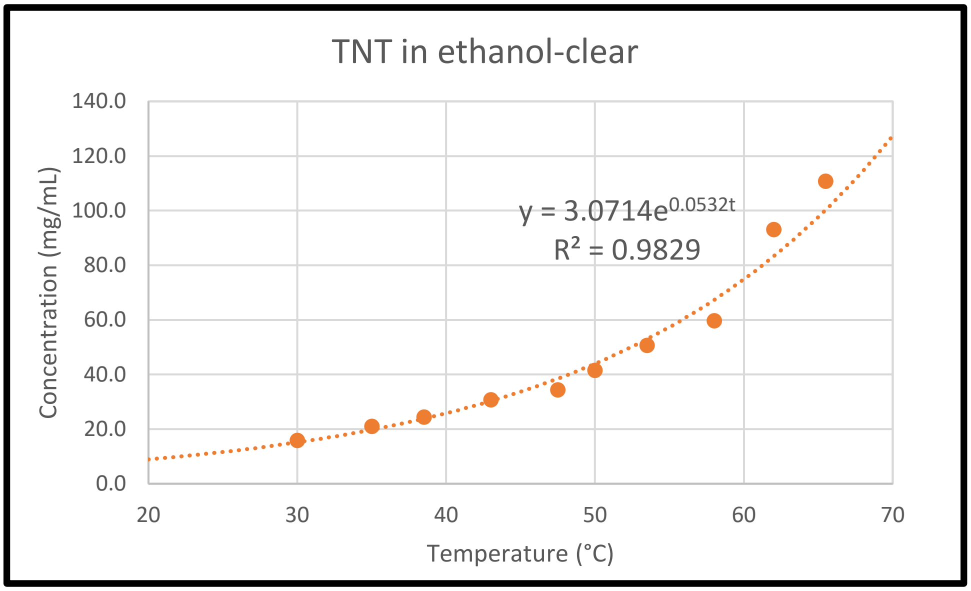


Figure 3
TNT solubility curves in ethyl acetate



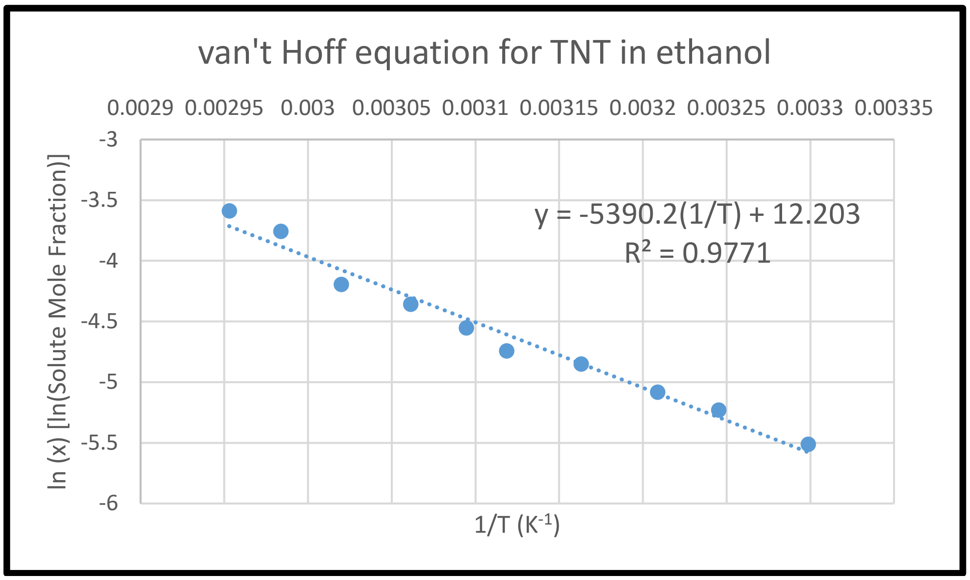
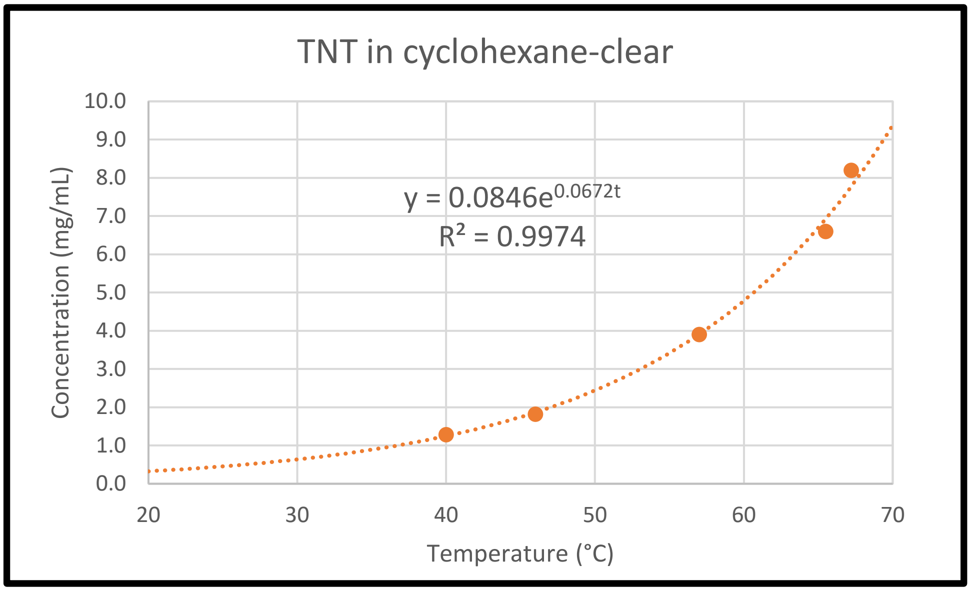


Figure 4
TNT solubility curves in ethanol



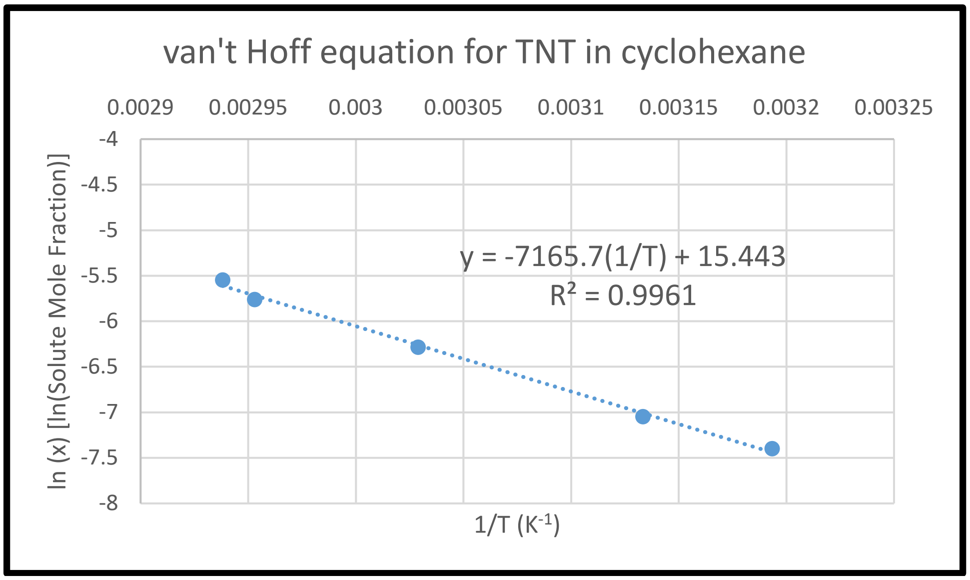
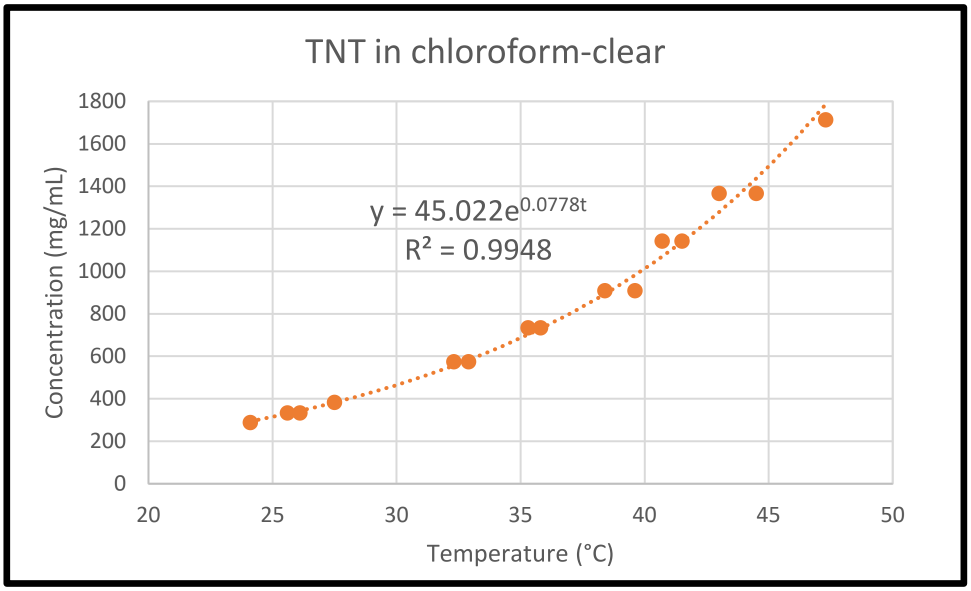


Figure 5
TNT solubility curves in cyclohexane



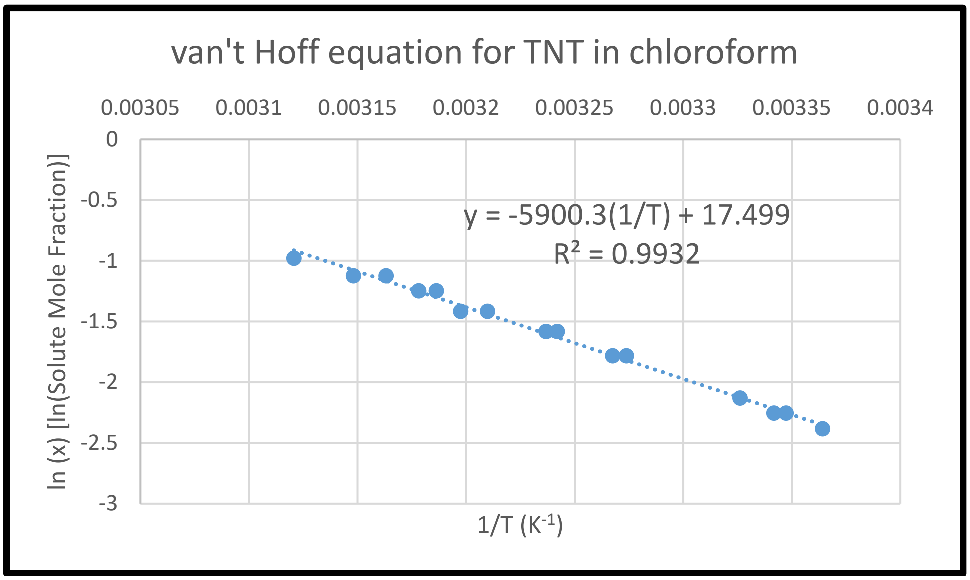


Figure 6
TNT solubility curves in chloroform

CONCLUSIONS

Solubility curves and van’t Hoff plots of 2,4,6-trinitrotoluene (TNT) were constructed for five solvents using the Avantium Crystal16™ parallel crystallizer. The solubility curves constructed were exponential in nature. The resulting regression lines show limited variation with all R^2 values greater than 0.9771. The solubility curves or van’t Hoff plots can be used to predict solubility at the temperature of interest.

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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.

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

Solubility Report of 2,4,6-Trinitrotoluene (TNT)	
Title	Project
Dr. Kelley Caflin	
Author/Project Engineer	Report number/Date received (to be completed by LCSD)
x2657 B3028	FCDD-ACM-EW
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