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SOLUBILITY REPORT OF 1-NITROPYRAZOLE (1-NP)

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U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND ARMAMENTS CENTER

Munitions Engineering Technology Center

Picatinny Arsenal, New Jersey

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14. ABSTRACT

Solubilities of 1-Nitropyrazole in six 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.

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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 1-Nitropyrazole (1-NP). Its chemical structure can be seen in figure 1. The solubility of 1-NP in various solvents was determined. The resulting solubility data can be used for synthesis, recrystallization, and formulation purposes.

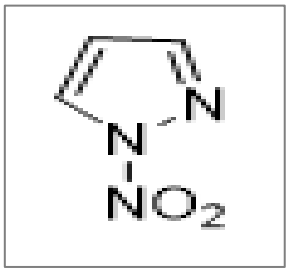


Figure 1
1-NP

EXPERIMENTAL SECTION

Materials

The 1-NP was synthesized at the U.S. Army Combat Capabilities Development Command Armaments Center, Picatinny Arsenal, NJ, and determined pure by both nuclear magnetic resonance, ultra performance liquid chromatography, and melting point. Solvents used for solubility experiments were purchased from commercial sources and used without further purification. They are as follows: dichlorobenzene NE Scientific Assay 99% Lot P975R, 1-propanol Sigma Aldrich ACS reagent Batch 79096MK, diethylene glycol Sigma Aldrich Reagent Plus 99% Batch 92996MJ, disopropyl ether Sigma Aldrich anhydrous 99% Lot SHBH0612V, 1,4 dioxane Sigma Aldrich anhydrous 99.8% Lot SHBJ1381, and sulfolane Sigma Aldrich 99% Lot MKBT2947V.

Solubility Measurements

Solubility measurements of 1-NP were acquired on an Avantium Crystal16™ and were analyzed using CrystalClear software. Solvents investigated were dichlorobenzene, 1-propanol, diethylene glycol, diisopropyl ether, 1,4 dioxane, and sulfolane. 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.

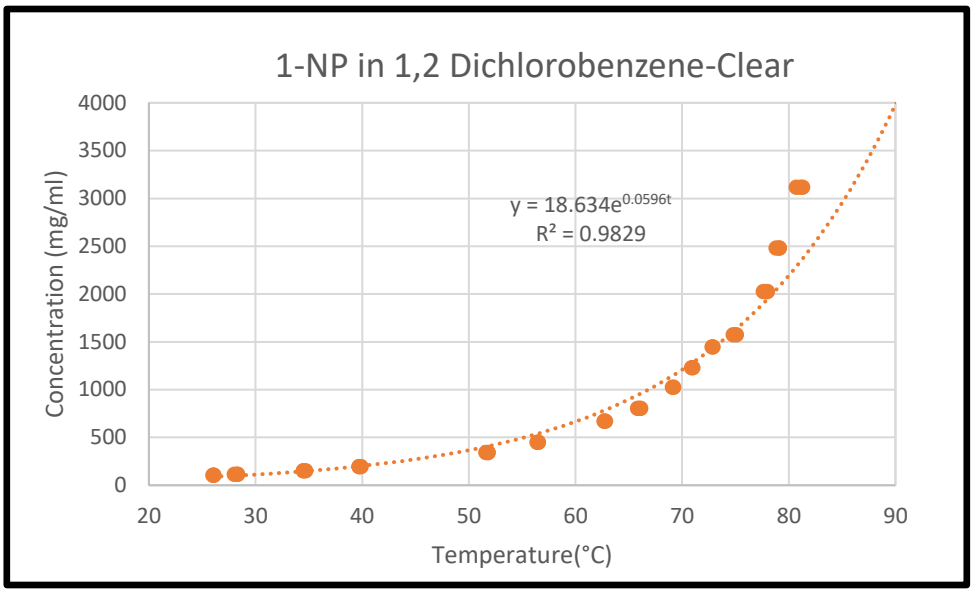
The solubility of each vial solution was determined by identifying clear point temperatures, which are defined as the temperature at which the turbidity of the solution decreases upon heating and the solution becomes transparent. Graphing the clear point temperatures versus the concentration of the solution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

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

where x is the solute mole fraction, ΔH is the dissolution enthalpy, T0 (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. Shown in figures 2 through 7 are the solubility curves of 1-NP in dichlorobenzene, 1-propanol, diethylene Glycol, diisopropyl ether, 1,4 dioxane, and sulfolane.



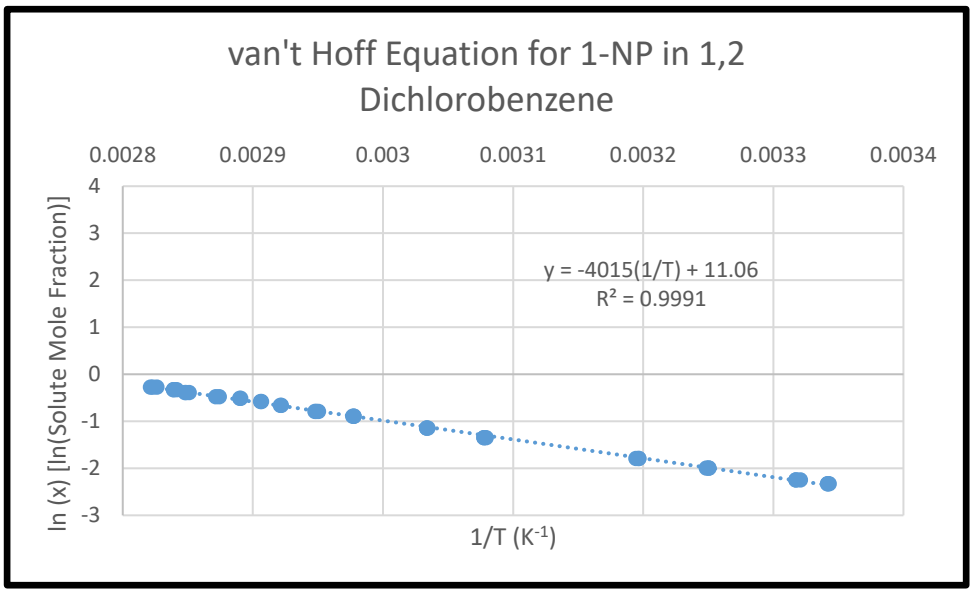
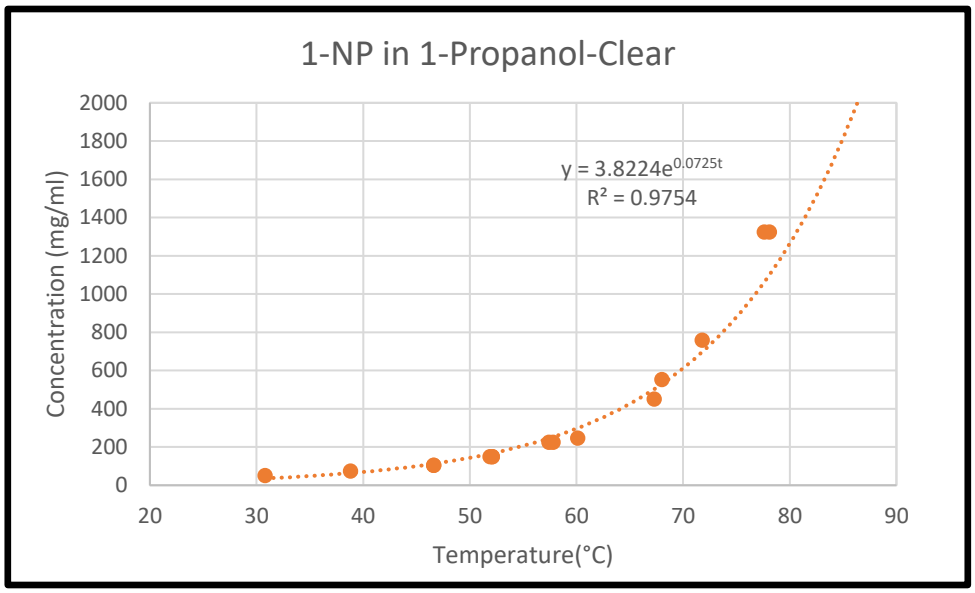


Figure 2
1-NP solubility curves in 1,2 dichlorobenzene



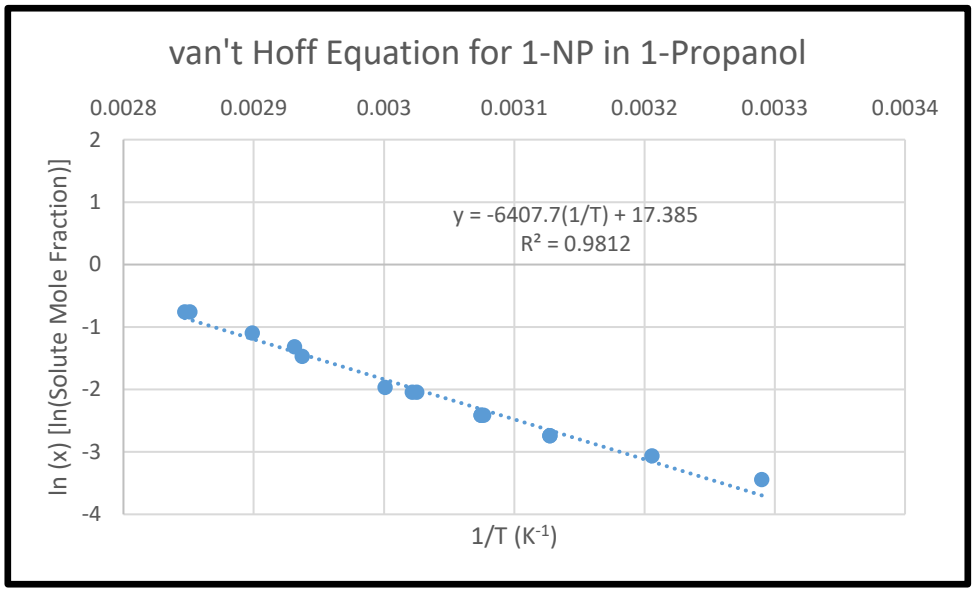
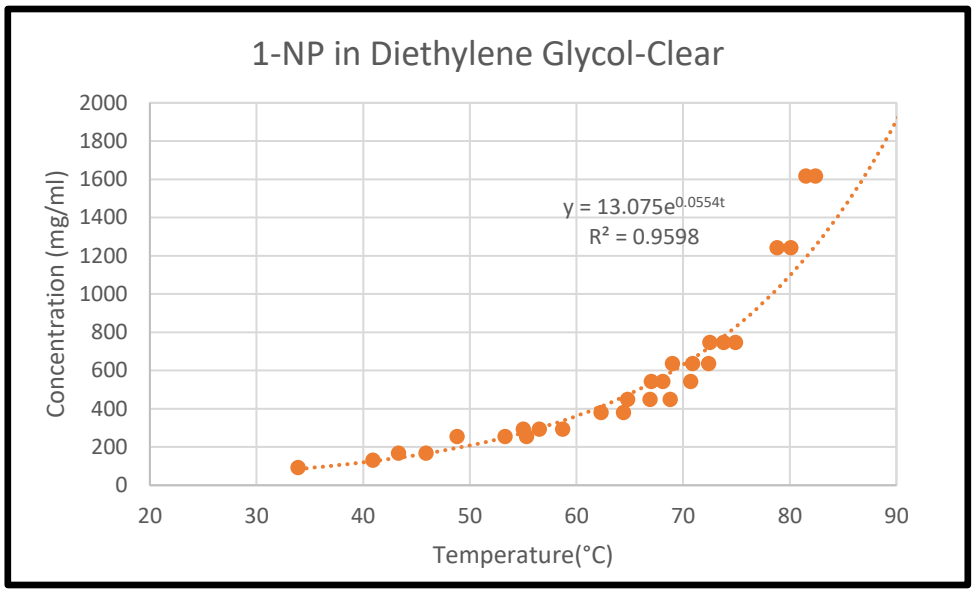


Figure 3
1-NP solubility curves in 1-propanol



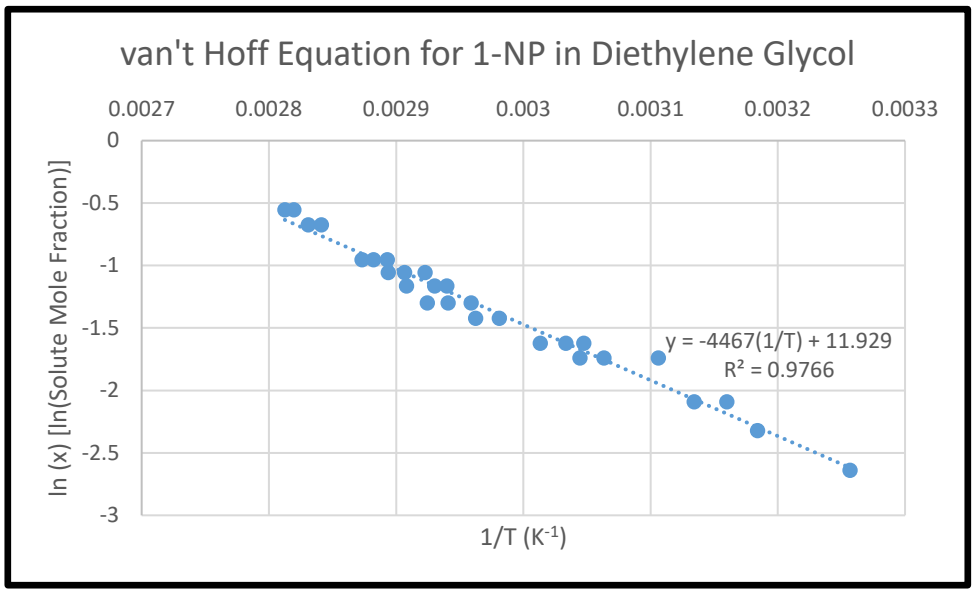
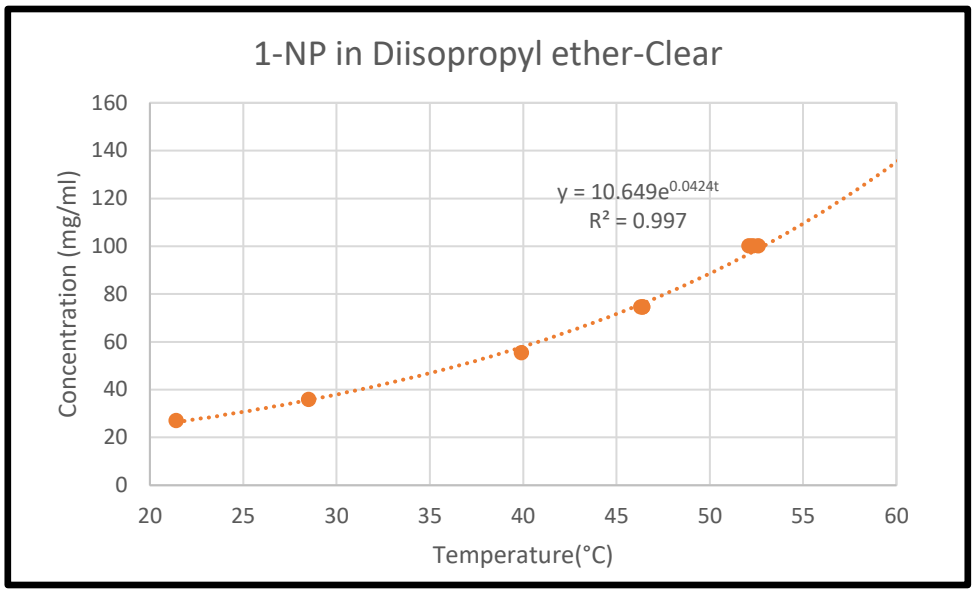


Figure 4
1-NP solubility curves in diethylene glycol



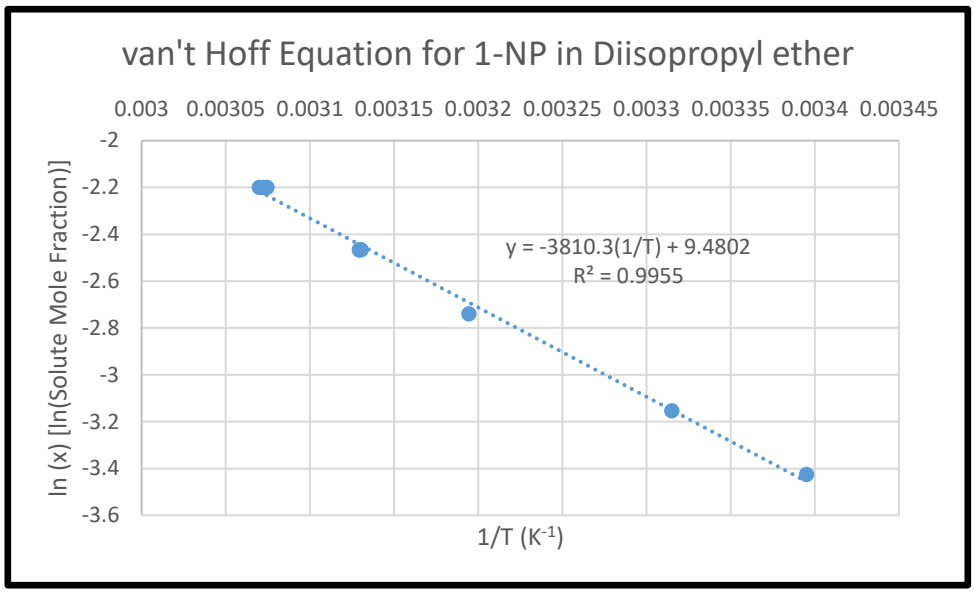
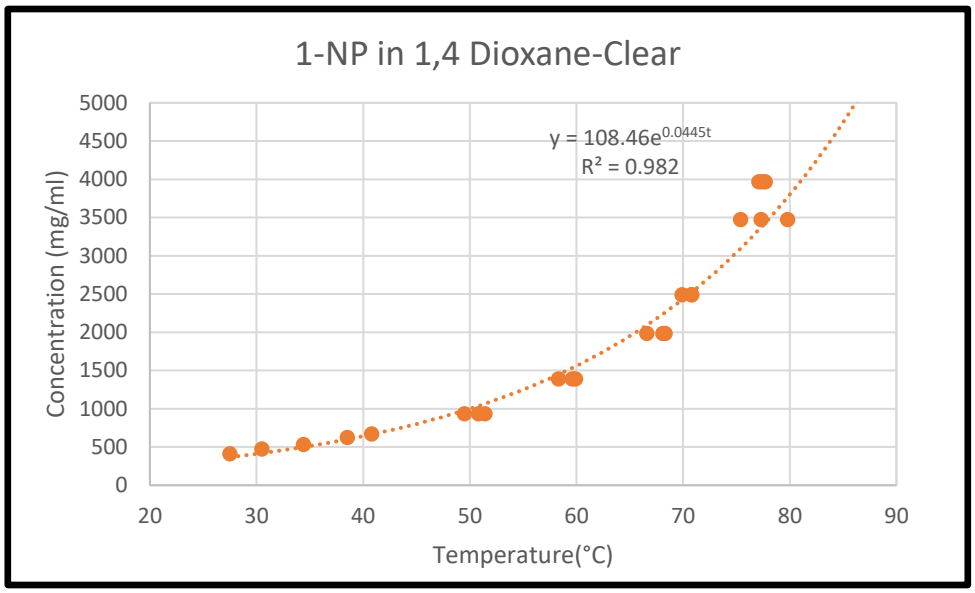


Figure 5
1-NP solubility curves in diisopropyl ether



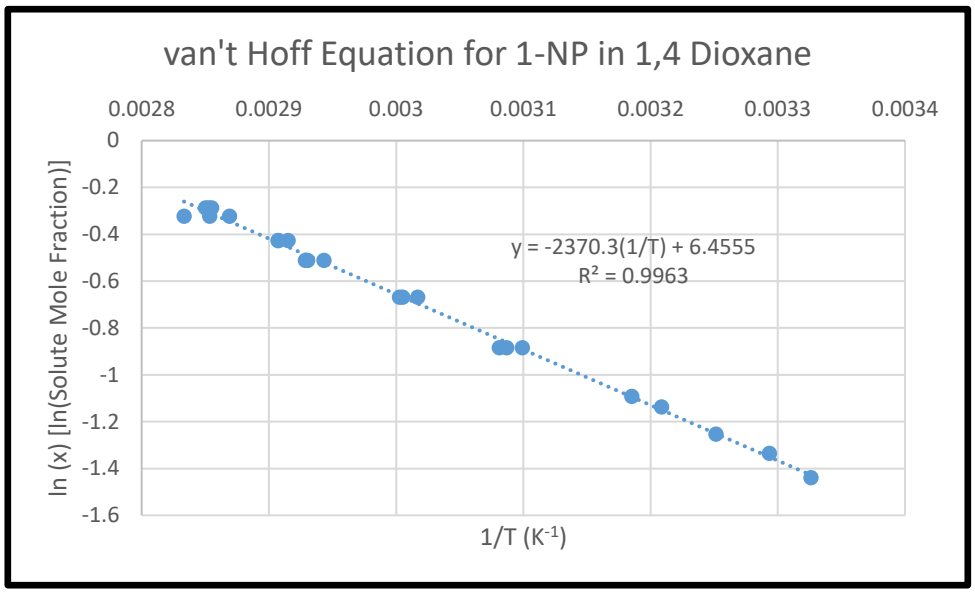
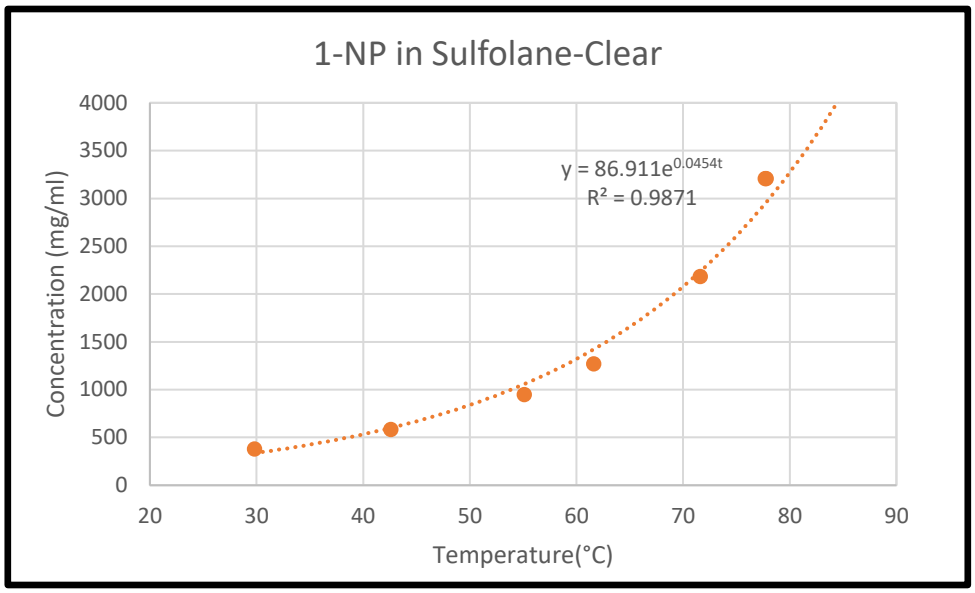


Figure 6
1-NP solubility curves in 1,4 dioxane



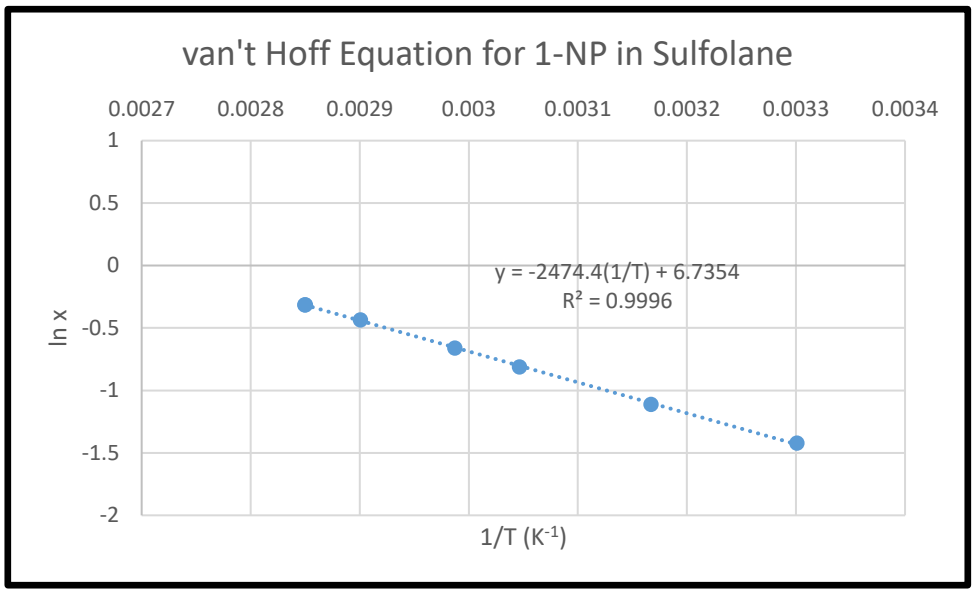


Figure 7
1-NP solubility curves in sulfolane

CONCLUSIONS

Solubility curves and van't Hoff plots of 1-Nitropyrazole were constructed for six 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 0.9598. The solubility curves or van't Hoff plots can be used to predict solubility at the 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.

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