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Solubility, Density, and Metastable Zone Width of the 3-Nitro-1,2,4-triazol-5-one + Water System

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The solubility of 3-nitro-1,2,4-triazol-5-one in water was measured over the temperature range from 284.65 K to 367.55 K. The results were correlated by an exponential equation. Densities of the aqueous solutions have been measured at temperatures from 308.15 K to 368.15 K and at mole fractions of 0.0027 to 0.014. The metastable zone width was measured for the evaluation of the nucleation rate. Results for the density and the metastable zone width were correlated by empirical equations.

Introduction

3-Nitro-1,2,4-triazol-5-one (NTO) is more attractive than common explosives such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2,4,6-trinitrotoluene (TNT) in terms of its insensitivity and stability (Lee and Coburn, 1985; Yi et al., 1993; Ostmark et al., 1993; Becuwe and Delclos, 1993). The structural formula of NTO is shown in Figure 1.

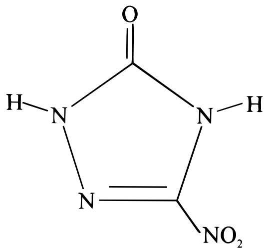

Figure 1. Structure of NTO.

The morphology of NTO crystals coming from the reaction process has typically a jagged rodlike shape, which is easy to agglomerate and ultimately becomes sensitive to a sudden shock. One of the ways to lower the sensitivity toward sudden shock is to control the crystal morphology to be close to spherical. On the other hand, the mother liquors contain additional components from the chemical reaction, in particular formic acid, nitric acid, sulfuric acid, and 1,2,4-triazole-5-one (Lee and Coburn, 1985; Yi et al., 1993). Some of these are trapped into the crystals and are present even after washing(Lee and Coburn, 1985). The purification process is necessary to remove these impurities. One attempt to solve these problems is by recrystallization of the NTO in a solvent that allows control of the crystal size and crystal shape, purity, and narrow crystal size distribution. To achieve an appropriate rate of crystallization in a cooling crystallizer, a solvent capable of dissolving NTO is required. A solvent to improve the crystal quality must be selected. Water is a suitable solvent in a cooling crystallizer from these points of view. The solubility of NTO must be known in order to interpret the kinetics of NTO recrystallization. Also the metastable zone width is an important factor to control the nucleation and hence the crystal size (Mersmann, 1994). There appear to be no previous measurements on the solubility, density, and metastable zone width for the (NTO + water) system.

In this study, the density, solubility, and metastable zone width for the NTO + water system were measured over wide ranges of temperatures and concentrations.

Experimental Section

Materials. NTO was from Hanwha Co., 99.5 mol % pure. The water used in this work was triple distilled. Before use, NTO was purified further by recrystallization in an analysis grade of methanol supplied by Merck. The NTO purified had purity > 99.93 mol %. Its purity was analyzed by ^{1}H NMR spectroscopy (JEOL FX90Q FT-NMR 90-MHz).

Measurement of Solubility. The mixtures were prepared by mass using a Mettler AG 204 balance with an accuracy of ±0.0001 g. The estimated accuracy in the mole fraction is less than $\pm 2 \times 10^{-4}$. The solubility of NTO in the water was measured using equipment previously described (Kim et al., 1994). The equilibrium cell, a cylindrical glass vessel (50 mm inside diameter, 120 mm long), was placed, by ground-glass joint, in a triple-jacketed vessel. The outer jacket was evacuated, and either heated or cooled medium from a thermostated bath could be circulated through the middle jacket. An ethylene glycol

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+ water solution was thermostated and controlled by a thermoelectric Eurotherm 808 PID controller with ±0.1 K accuracy. The cell had a perforated rubber stopper, through which a copper-constantan thermocouple was inserted. The contents were stirred with a magnetic spin bar. The cell was tightly sealed to protect the system from dust and moisture condensation. Mixtures of solute and solvent were cooled in bath until an abundant amount of crystal was formed and then heated very slowly at less than 0.001 K min^{-1} near the equilibrium temperature. The crystal disappearance temperature, detected visually, was measured with a calibrated thermocouple connected to a recorder (Yokogawa, 180 micro R). The thermocouples were calibrated with a calibrated thermometer from Fisher Scientific (No. 15-078-7) with an accuracy of ±0.05 K. The accuracy of the thermocouple measurements is believed to be ±0.1 K. Some of the experiments were conducted in triplicate to check the reproducibility. The saturation temperature for a given mixture was reproducible within ±0.1 K.

Measurement of Density. The density of aqueous solutions of NTO has been determined using a digital densimeter (Mettler Toledo, AG) with density measurement packages (No. 210260 and No. 238491), which uses the Archimedes' principle. The density of solution was determined using a sinker of known volume (10 mL). The sinker was weighed in air and then in the solution. The density can be determined by dividing buoyancy of the sinker in the solution by the volume of the sinker from the two weighings and by correcting for the air buoyancy (0.0012 g cm^{-3}) that results from the fact that a solid body like a sinker experiences air buoyancy (0.0012 g per cm^3 volume of the body) in the weighing in air. An electronic balance (Mettler AG) in the densimeter allows for direct determination of the buoyancy. The densimeter was interfaced to a computer. Before measurement, the densimeter was calibrated with distilled water at the experimental temperatures. Some of the experiments were conducted to check the accuracy at the end of measurement. The densimeter in the above configuration appeared to have an accuracy of ±0.0002 g cm^{-3}. The bath temperature was measured with a calibrated thermocouple and maintained constant to ±0.1 K at the desired temperature.

Measurement of Metastable Zone Width. The metastable zone width was measured by the polythermal method(Kim and Ryu, 1997). The equipment was similar to that used in measurement of solubility with minor modifications. A solution with known composition was placed into a thermostated nucleation cell in a 300 mL cylindrical glass vessel (90 mm inside diameter, 120 mm long) fitted with a triple jacket and agitated by a magnetic bar. Its temperature was gradually lowered at a constant cooling rate until the first crystals appeared and then raised at rate of 0.001 K min^{-1} until the crystals dissolved. The difference between the two temperatures is called metastable zone width. The consistency of the crystal disappearance temperature was checked by comparison of the saturation temperature obtained in solubility measurements with mixtures of exactly known composition. The experimental data were in satisfactory agreement with the results from solubility measurements with ±0.2 K accuracy.

For NTO the enthalpy of fusion, $\Delta_{\mathrm{fus}}H = 92.8$ kJ mol^{-1} at the melting temperature, $T_{\mathrm{m}} = 547.9$ K, was determined by differential scanning calorimetry (DSC; Mettler) with an accuracy of ±0.05 kJ mol^{-1}. NTO has a crystal density of 1930 kg $\mathrm{m}^{-3}$and a molecular weight of 130 (Lee and Coburn, 1985; Yi et al., 1993; Ostmark et al., 1993; Becuwe and Delclos, 1993).

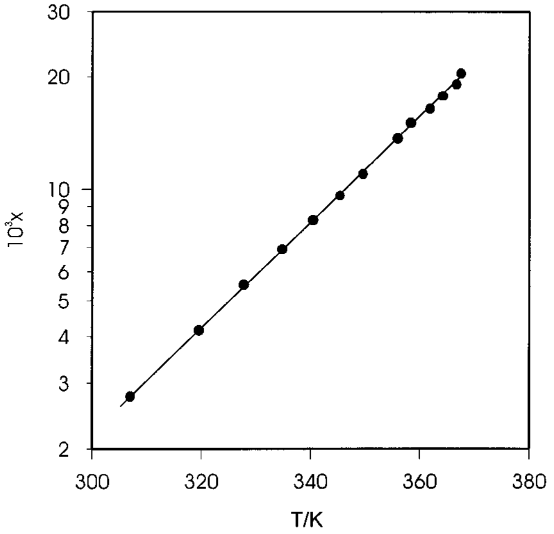

Figure 2. Mole fraction solubility of NTO in water.

Table 1. Experimental Mole Fraction Solubility *x* of NTO in Water

x	*T*/K	*x*	*T*/K
0.001 383	284.65	0.012 308	351.85
0.002 762	307.05	0.013 657	356.05
0.004 137	319.65	0.015 002	358.45
0.005 508	327.95	0.016 344	361.95
0.006 875	334.85	0.017 682	364.25
0.008 239	340.55	0.019 016	366.75
0.009 599	345.45	0.020 347	367.55
0.010 956	349.65		

Results and Discussion

Solubility. The solubility of NTO in water was measured over the temperature range from 284.65 K to 367.55 K, and the values are listed in Table 1 and plotted in Figure 2. It was found that an exponential temperature dependence, as shown in Figure 2, permitted a linear interpolation. Thus, the mole fraction solubility x of NTO was analyzed using the equation

$$x = \alpha\, \mathrm{e}^{\beta(T/\mathrm{K})} \tag{1}$$

where T is the absolute temperature and α and β are parameters. The linear expression describes satisfactorily the temperature dependence of the solubility, within the temperature range studied. The relative standard deviation and the average deviations between the measured solubility data and the data calculated from eq 1 were 0.01 and 7.72×10^{-5}, respectively. The values of α and β are 1.429×10^{-7} and 0.0322 K^{-1}, respectively. The relative standard deviations σ is defined by

$$\sigma = \left[\frac{1}{N}\sum\left(\frac{x(\mathrm{calc}) - x}{x}\right)_i^2\right]^{1/2} \tag{2}$$

and the absolute average deviation Δ is defined by

$$\Delta = \frac{1}{N}\sum|(x(\mathrm{calc}) - x)_i| \tag{3}$$

where N is the number of data points.

To calculate the enthalpy of dissolution of NTO crystals in the solvent, the interaction of a solvent and solute can

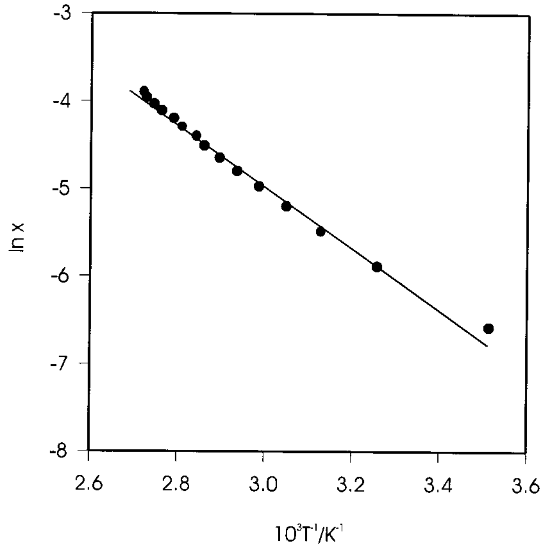

Figure 3. Plots of ln mole fraction solubility versus T^{-1}.

be expressed as the following ideal theory (Prausnitz et al., 1986)

$$\ln x = \frac{-\Delta_{\mathrm{sol}}H}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right) \tag{4}$$

where x is the mole fraction of solute, $\Delta_{\mathrm{sol}}H$, is the enthalpy of dissolution of NTO, and T is the equilibrium temperature. $\Delta_{\mathrm{sol}}H$ is equal to $\Delta_{\mathrm{fus}}H$ for an ideal system and $\Delta_{\mathrm{fus}}H + \Delta_{\mathrm{mix}}H$ for a nonideal system. The enthalpy of mixing, $\Delta_{\mathrm{mix}}H$, is a measure for the solute−solvent interaction, whereas the enthalpy of fusion $\Delta_{\mathrm{fus}}H$ is solvent independent. When the solubility curve is known, $\Delta_{\mathrm{sol}}H$ and thus $\Delta_{\mathrm{mix}}H$ can be determined when $\Delta_{\mathrm{fus}}H$ is known. The solubility of NTO in water can generally fitted to eq 4. Figure 3 shows the relationship between ln x_1 and $1/T$. All data show an approximately straight line with a slight curvature. From Figure 3, the enthalpy of dissolution was calculated by the least-squares method and was found to be 31.6 kJ mol^{-1}. The enthalpy of mixing $\Delta_{\mathrm{mix}}H$ of water is therefore calculated to be −61.2 kJ mol^{-1}. Such a large $\Delta_{\mathrm{mix}}H$ shows a large solvent−solute interaction, and this could have a large effect on morphology because the difference between interactions with certain crystal surfaces could be also large.

Density of Aqueous Solution of NTO. The densities for the NTO + water system were measured in the range of 308.15 K to 368.15 K and in mole fraction from 0.0027 to 0.014. Only the average values of the densities from three independent measurements for five concentrations are listed in Table 2 and plotted in Figure 4. The experimental data were fitted to eq 5 as a function of absolute temperature, T, and NTO mole fraction, x:

$$\rho/(\mathrm{kg\ m}^{-3}) = k_1 + k_2x + k_3(T/\mathrm{K}) + k_4x(T/\mathrm{K}) \tag{5}$$

The values of coefficients k_1, k_2, k_3, and k_4 of eq 5 describing densities, ρ, are 1166.74, 427.75, −0.5508, and 5.9576, respectively. The relative standard deviation and the average absolute deviation between the measured density data and calculated data were 0.0006 and 0.04 kg m^{-3}, respectively.

Metastable Zone Width. The most readily available method that is used for determining the degree of nucleation is the measurement of the metastable zone width at different cooling rate (Nyvlt, 1968, 1980; Kim and Ryu, 1997). The principle of the method is based on the fact that the rate of saturation on reaching the boundary of the metastable zone is equal to the rate of nucleation. Therefore the metastable zone width is regarded as one of nucleation characteristics revealed macroscopically. For nucleation from solution cooled at a constant rate, the relationship between the maximum allowable undercooling (i.e., metastable zone width), $\Delta T_{\max}$, and cooling rate, b, is as follows (Nyvlt, 1968; Kim and Ryu, 1997)

$$\log b/(\mathrm{K\ min}^{-1}) = \log k_n + n \log(\Delta T_{\max}/\mathrm{K}) \tag{6}$$

where k_n is a constant related to nucleation rate and n is the nucleation order.

This equation indicates that the dependence of log b on log $\Delta T_{\max}$ is linear, and the slope of the line is the order of the nucleation process. The metastable zone width, $\Delta T_{\max}$, was taken as the difference between the equilibrium temperature and the temperature at which nuclei were detected for each particular cooling rate. The equilibrium temperature was obtained from the experimentally determined solubility curve.

Metastable zone widths for saturation temperature and cooling rate are listed in Table 3 and are plotted in log−

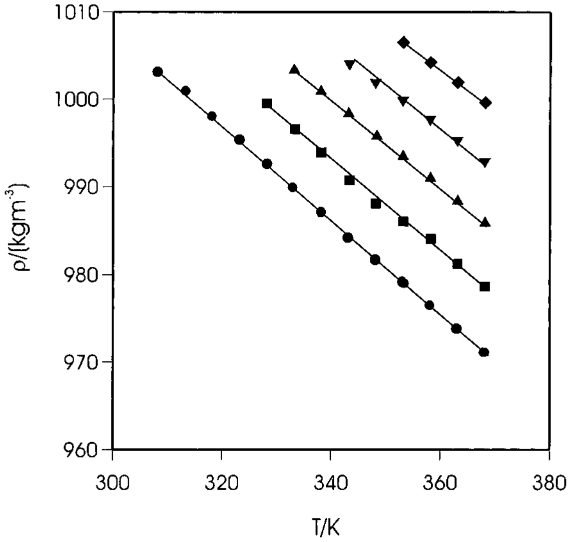

Figure 4. Density of NTO aqueous solutions as a function of mole fraction x: (●) $x = 0.002\ 762$, (■) $x = 0.005\ 508$, (▲) $x = 0.008\ 249$, (▼) $x = 0.010\ 956$, (◆) $x = 0.013\ 657$.

Table 2. Experimental Densities for xNTO + (1 − x)H$_2$O

10^2x	T/K	ρ/(kg m^{-3})	10^2x	T/K	ρ/(kg m^{-3})
0.2762	308.15	1003.3	0.5508	363.15	981.1
0.2762	313.35	1000.8	0.5508	368.15	978.5
0.2762	318.15	997.9	0.8239	333.15	1003.2
0.2762	323.15	995.2	0.8239	338.15	1000.8
0.2762	328.15	992.5	0.8239	343.15	998.3
0.2762	333.15	989. 8	0.8239	348.15	995.8
0.2762	338.15	987.0	0.8239	353.15	993.7
0.2762	343.15	984.1	0.8239	358.15	990.9
0.2762	348.15	981.6	0.8239	363.15	988.3
0.2762	353.15	979.1	0.8239	368.15	985.8
0.2762	358.15	976.4	1.0956	343.15	1003.9
0.2762	363.15	973.7	1.0956	348.15	1002.1
0.2762	368.15	971.0	1.0956	353.15	999.9
0.5508	328.15	999.4	1.0956	358.15	997.6
0.5508	333.15	996.4	1.0956	363.15	995.2
0.5508	338.15	993.8	1.0956	368.15	992.8
0.5508	343.15	990.6	1.3657	353.15	1006.5
0.5508	348.15	988.0	1.3657	358.15	1004.2
0.5508	353.15	985.9	1.3657	363.15	1001.9
0.5508	358.15	984.0	1.3657	368.15	999.6

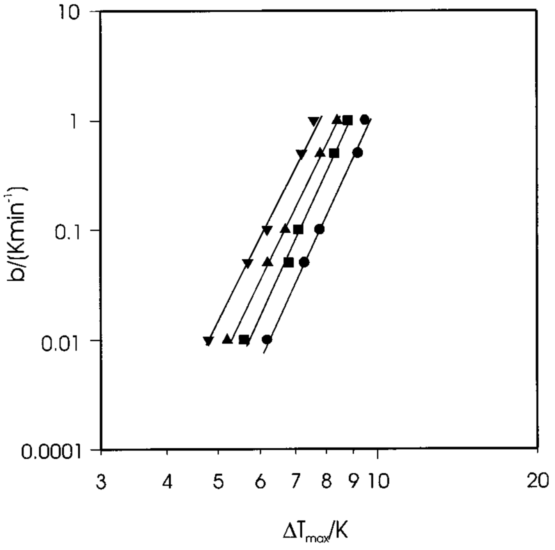

Figure 5. Plots of b versus ΔT_{max}: (●) T_s = 338.15 K, (■) T_s = 348.15 K, (▲) T_s = 358.15 K, (▼) T_s = 368.15 K.

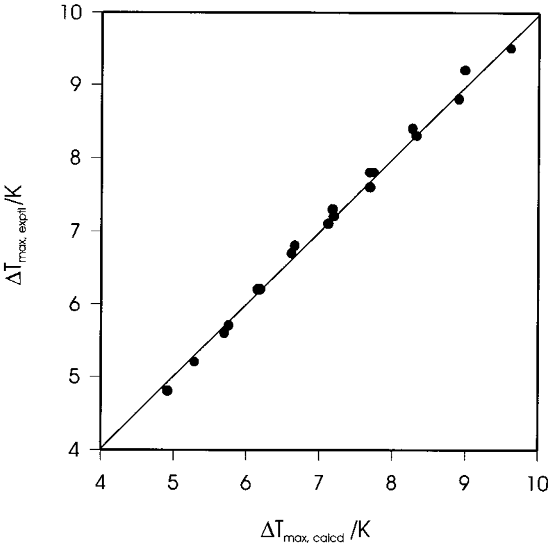

Figure 6. Comparison between the experimental data and the calculated data in eq 7.

Table 3. Metastable Zone Width Measurements

	$\Delta T_m/K$			
b/ (K min^{-1})	T_s = 338.15K	T_s = 348.15 K	T_s = 358.15 K	T_s = 368.15 K
0.01	6.2	5.6	5.2	4.8
0.05	7.3	6.8	6.2	5.7
0.1	7.8	7.1	6.7	6.2
0.5	9.2	8.3	7.8	7.2
1	9.5	8.8	8.4	7.6

Table 4. Values of Nucleation Parameters in Eq 6

T_s/K	k_n	n	Δ/K	σ
338.15	2.96×10^{-10}	9.692	0.2071	0.0280
348.15	8.61×10^{-10}	9.582	0.1498	0.0271
358.15	7.05×10^{-9}	8.811	0.1345	0.0276
368.15	1.24×10^{-8}	8.789	0.1444	0.0245

log coordinates in Figure 5. The plots are found to give a good straight line. These results show that the metastable zone width of the aqueous NTO solutions increases with the cooling rate for all the experimental conditions explored. The width of the metastable zone also increases with decreasing saturation temperature. The values of the order of nucleation rate, n, and the constant of nucleation rate, k_n, of eq 6 were evaluated by regression analysis from the slopes and intercepts found in Figure 5 and are shown in Table 4 with the relative standard deviation and average absolute deviation. The order of the nucleation rate is in the range between 8 and 9 and appears to be dependent on the saturation temperature.

As shown in Figure 5, the metastable zone width varies with the cooling rate, b, and the saturation temperature, T_s. The relationship among them can be expressed as the following relation:

$$\Delta T_{max}/\mathrm{K} = c_1 b^l (T_s/K)^m \qquad (7)$$

The values of parameters c_1, l, and m obtained in this study are 7.79×10^7 K^{1-l-m} min^l, 0.0971, and -2.731, respectively. All results were correlated with eq 7, shown in Figure 6. The relative standard deviation and the average absolute deviation between the measured metastable zone width data and calculated data were 0.083 and 0.065 K, respectively. Therefore, eq 7 expresses the metastable zone width in which the variation of the cooling rate and initial concentration in such a cooling crystallizer are considered.

Conclusion

Data have been obtained on the solubility, density and metastable zone width for the NTO + water system at the temperatures from 284.65 K to 368.15 K and at mole fractions of NTO from 0.0014 to 0.02. These data are well correlated the empirical relations described in this study. The solubility of NTO in water shows a high dependence on temperature. These results show that NTO recrystallization can be carried out effectively by cooling crystallization. In particular, the metastable zone width is useful to clarify the kinetics of nucleation and crystal growth in a crystallization process.

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