Solubility of 1,1-Diamino-2,2-dinitroethylene in *N*,*N*-Dimethylformamide, Dimethyl Sulfoxide, and *N*-Methyl-2-pyrrolidone

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The solubility of 1,1-diamino-2,2-dinitroethylene in dimethyl sulfoxide, *N*,*N*-dimethyl formamide, and *N*-methyl-2-pyrrolidone was measured by a polythermal method in the temperature range of (293.15 to 363.15) K. The solubility data were correlated against temperature with an exponential equation. The enthalpy of dissolution in each solvent was calculated from the temperature dependence.

Introduction

In 1998, DADNE (1,1-diamino-2,2-dinitroethylene, Figure 1) was synthesized from hydrolysis and mixed-acid nitration of 2-methyl-4,6-pyrimidinedion by Latypov.[1] Further characterization showed that DADNE has significantly lower sensitivity to the hazardous stimuli, in particular, impact and friction, than RDX (1,3,5-trinitroperhydro-1,3,5-triazine) and has energetic performance similar with commercial high explosives.[2] Because of those insensitive characteristics, DADNE has been extensively studied as a promising crystalline energetic material for LOVA (low vulnerability ammunition) compositions.[3,4]

In general, crystal properties of energetic compounds including crystal shape, size and size distribution, and polymorph strongly influence the combustion rate and ballistic characteristics of the propulsion system. Therefore, DADNE is often recrystallized from supersaturated solution to control those properties. Thus, it is definitely necessary to know the solubility of DADNE in different solvents to determine the best solvents and to optimize the crystallization operation.[5]

DADNE has been known to have poor solubility in ordinary organic solvents but is readily soluble in dipolar aprotic solvents.[6,7] However, to date, no systematic study of DADNE has been published. In this work, solubilities of DADNE in DMSO (dimethyl sulfoxide), DMF (*N*,*N*-dimethylformamide), and NMP (*N*-methyl-2-pyrrolidone) were measured in the temperature range of (293.15 to 363.15) K, and the enthalpies of dissolution for DADNE were calculated from those solubility data.

Experimental Section

Reagents and Apparatus. DADNE was kindly provided by Hanwha Corp. (Korea). DMSO, NMP, and DMF were purchased from Aldrich Co. (USA). All chemicals of reagent grade were used without further purification. Prior to solubility measurements, raw DADNE was purified by the following steps: at room temperature, solid DADNE was gently dissolved in DMSO with a mass ratio of 1:3. That solution was filtered through a sintered ceramic filter with a pore diameter of (4 to 5) μm to remove all impurities suspended in the solution. Then, recrystallization of DADNE was performed by addition of distilled water into the DADNE + DMSO solution. DADNE crystals were recovered from a ceramic filter which was directly connected to a vacuum pump. Recrystallization of DADNE was repeated three times, and finally DADNE crystals were dried with a convection oven at 353 K and then sealed in a sample vial for solubility measurements.

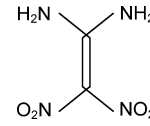

Figure 1. Chemical structure of 1,1-diamino-2,2-dinitroethylene.

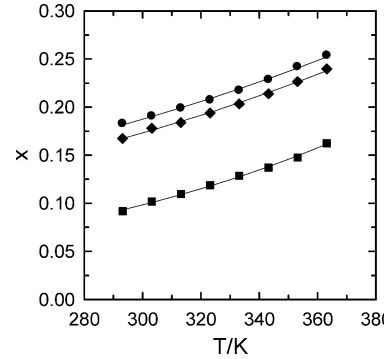

Figure 2. Solubility of DADNE in three solvents as different temperatures: ●, DMSO; ■, DMF; ◆, NMP; −, calculated by eq 1.

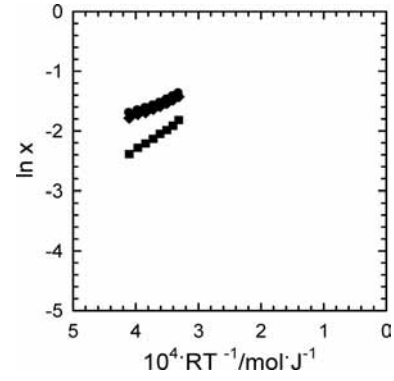

Figure 3. Plot of experimental solubility (x) versus $10^4/RT$: ●, DMSO; ■, DMF; ◆, NMP; −, calculated by eq 4.

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Table 1. Experimental Solubility (x) and Calculated Solubility (x^{calc}) of DADNE in DMSO (1), DMF (2), and NMP (3)

T/K	x_1	x_1^{calc}	100δ	x_2	x_2^{calc}	100δ	x_3	x_3^{calc}	100δ
293.15	0.1828	0.1814	0.7585	0.0918	0.0932	–1.5776	0.1675	0.1673	0.1041
303.15	0.1906	0.1902	0.2232	0.1020	0.1008	1.1002	0.1780	0.1759	1.1475
313.15	0.1989	0.1993	–0.2311	0.1096	0.1091	0.5283	0.1839	0.1850	–0.5988
323.15	0.2073	0.2089	–0.7659	0.1186	0.1180	0.5511	0.1938	0.1945	–0.3760
333.15	0.2173	0.2189	–0.7850	0.1286	0.1276	0.7941	0.2033	0.2046	–0.6175
343.15	0.2286	0.2295	–0.3884	0.1370	0.1380	–0.6887	0.2138	0.2151	–0.5974
353.15	0.2418	0.2406	0.5186	0.1477	0.1493	–1.1238	0.2267	0.2262	0.2176
363.15	0.2537	0.2522	0.6191	0.1624	0.1615	0.5140	0.2398	0.2379	0.8076

Table 2. Regression Parameters of Equation 1

solvent	A	B	σ
DMSO	0.045735	0.004701	$1.2538 \cdot 10^{-3}$
DMF	0.009323	0.007854	$1.0898 \cdot 10^{-3}$
NMP	0.038326	0.005027	$1.2820 \cdot 10^{-3}$

Table 3. Enthalpy of Dissolution ($\Delta_{diss}H$) Obtained from Equation 4

solvent	$\Delta_{diss}H$/(kJ·mol^{-1})
DMSO	−4.144
DMF	−6.955
NMP	−4.435

Experimental Procedure. The solubility of DADNE in each solvent was measured by a polythermal method described by Nyvlt.[4] Initially, the mass of the solute was carefully measured by an electronic analytical balance (AG204, Mettler-Toledo, USA) with an uncertainty of ± 0.1 mg. The solute + solvent mixture in proportions equivalent approximately to a saturated composition was slowly loaded into the double-jacketed vessel which was maintained in the middle of the proposed temperature range by circulating water/ethylene glycol solution (1:3, mass ratio) from a thermostat (Julabo FP40, Germany). DADNE crystals were violently stirred by a magnetic bar, and a K-type thermocouple was inserted to measure the temperature of the DADNE solution. The solution temperature was increased slowly until the last DADNE crystals dissolved. At this point, the equilibrium saturation was assumed to be achieved. The clear solution was cooled until the visible appearance of DADNE crystals. Then, the temperature was increased repeatedly until the last DADNE crystal disappeared. Experimental runs were carried out three times to confirm the reproducibility, and their average values were used.

Results and Discussion

Solubility. Experimental solubilities of DADNE in DMSO, NMP, and DMF in the temperature range of (293.15 to 363.15) K are listed in Table 1. Figure 2 shows that DADNE solubilities in all solvents are exponentially increased in the temperature range of the experiments. Therefore, solubilities of DADNE were correlated with the following equation

$$x = A\mathrm{e}^{B(T/\mathrm{K})} \tag{1}$$

where x is the measured mole fraction. A and B are parameters of the exponential expression. The relative deviation (δ) is

$$\delta = \frac{(x - x^{calc})}{x} \tag{2}$$

where x^{calc} represents calculated solubility from eq 1. The root-mean-square deviation (σ) is

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}(x_i - x_i^{calc})^2}{N}} \tag{3}$$

where x_i represents experimental solubility and x_i^{calc} represents the calculated solubility from eq 1. N is the number of experimental points. From Table 1, eq 1 fits well with experimental solubility within a relative deviation of ± 1.5 %. Table 2 represents regression parameters of A and B in eq 1 for all solvents used.

Enthalpy of Dissolution. If solute and solvent form an ideal solution, we can predict the solubility from the van't Hoff equation. However, if the solution exhibits nonideality behavior, the enthalpy of fusion ($\Delta_{fus}H$) is replaced by the enthalpy of dissolution ($\Delta_{diss}H$).[8] The enthalpy of dissolution ($\Delta_{diss}H$) for DADNE can be calculated from

$$\ln x = \frac{-\Delta_{diss}H}{R(T/\mathrm{K})} + \frac{-\Delta_{diss}S}{R} \tag{4}$$

where $\Delta_{diss}H$ indicates the enthalpy of dissolution; $\Delta_{diss}S$ is the entropy of dissolution; R is the gas constant; and T is absolute temperature. Figure 3 displays a plot of x vs $(RT)^{-1}$ and yields a straight line. The enthalpy of dissolution ($\Delta_{diss}H$), shown in Table 3, is calculated from the slope.

Conclusions

Using a polythermal method, solubilities of DADNE in DMF, DMSO, and NMP were measured in the temperature range of (293.15 to 363.15) K. The solubility of DADNE was found to increase exponentially with temperature in all solvents considered. Experimental results show that the order of the solubility is followed as: DMSO > NMP > DMF. According to regression analysis of measured solubility data, the enthalpy of dissolution was calculated to be −4.144 kJ·mol^{-1} for DMSO, −4.435 kJ·mol^{-1} for NMP, and −6.955 kJ·mol^{-1} for DMF, respectively.

Literature Cited

(1) Latypov, N. V.; Bergman, J.; Langlet, A.; Wellmar, U.; Bemm, U. Synthesis and Reactions of 1,1-Diamino-2,2-Dinitroethylene. *Tetrahedron* **1998**, *54*, 1125–1136.

(2) Bemm, U.; Ostmark, H. 1,1-Diamino-2,2-Dinitroethylene: A Novel Energetic Material with Infinite Layers in Two Dimensions, Acta Crystallographica, Section C. *Cryst. Struct. Commun.* **1998**, *C54*, 1997–1999.

(3) Lochert, I. J. FOX-7 - A New Insensitive Explosive, DSTO-TR-1338, Defence Science and Technology Organisation, Australia, 2001.

(4) Cudzilo, S.; Chylek, Z.; Diduszko, R. Crystallization and Characterization of 1,1-Diamino-2,2 -Dinitroethylene (DADNE). *Biul. Wojesk. Akad. Tech.* **2005**, *54* (5−6), 5–17.

(5) Mullin, J. W. *Crystallization*, 4th ed.; Butterworth-Heinemann: Boston, 2001.

(6) Fuhr, I.; Heintz, T.; Kroeber, H. Product Design of Energetic Materials, *The seventh Italian Conference on Chemical & Process Engineering*, May 15−18, Giardini di Naxoa, Italy, 2005.

(7) Orzechowski, A.; Powala, D.; Florczak, B.; Maranda, A.; Nowaczewski, J. *Optimization of Crystallization of 1,1-Diamino-2,2-Dinitroethylene, New Trends in Research of Energetic Materials*; Pardubice: Czech Republic, April 19−21, 2006.

(8) Belny, D. H. M.; Mullin, J. W. Solubilities of Higher Normal Alkanes in m-Xylene. *J. Chem. Eng. Data* **2006**, *32*, 9–10.

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