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Solubility of Cyclotrimethylenetrinitramine (RDX) in Binary Solvent Mixtures

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Experimental solubilities of cyclotrimethylenetrinitramine (RDX) in binary solvent mixtures, such as γ-butyrolactone + water, cyclohexanone + water, *N*-methyl pyrrolidone + water, and acetone + water, were measured over the temperature range of 273.15 K to 363.15 K. The enthalpy of dissolution was determined experimentally from the solubility data.

Introduction

Cyclotrimethylenetrinitramine (RDX) is an explosive compound which is used in the mining and oil drilling industries and for military applications. Its chemical structure is shown in Figure 1. A good product performance is achieved by making a high solid load explosive with a low sensitivity to minimize an unintentional initiation of the explosive. The sensitivity is affected by crystal properties such as size, shape, and defects,[1] on which the solvent used in the crystallization process has a large influence. To reduce defects in the RDX crystal, optimum crystallization conditions were studied in various solvents.[2]

The solvent can substantially change the morphology of RDX crystals when it specifically interacts with certain RDX crystal faces. Crystallization is performed to determine experimentally the morphology of RDX crystals in the solvents.[3−7] There are various crystallization modes able to make a supersaturation such as cooling, evaporating, and drowning-out. The first step to determine the crystallization mode is to measure solubility in solvents capable of dissolving RDX. In drowning-out crystallization, water as a nonsolvent plays an important role for generating the supersaturation, which is a key parameter in determining the defects.[2,3,5] However, data for solubility of RDX, required to select the appropriate solvent, have not been presented. It is clear that the solubilities of all the chemical components produced in the crystallization need to be considered for solvent selection and operation of process. Binary solvents including water must be considered from these points of view.

The objective of the present work is to quantify the solubility characteristics of RDX in binary solvents as a function of temperature.

Experimental Section

Materials. RDX was from Hanwha Co., with a mole fraction purity of 99.9 %. All samples of RDX were used without further purification. The solvents used such as γ-butyrolactone, *N*-methyl pyrrolidone, cyclohexanone, and acetone were of analytical purity grade (purchased from Aldrich), and redistilled deionized water was used throughout.

Measurement of Solubility. The solubilities of RDX in the binary solvent mixtures, such as γ-butyrolactone + water, cyclohexanone + water, *N*-methyl pyrrolidone + water, and acetone + water, were measured by the isothermal method. They were determined in the vessel equipped with an FBRM (focused beam reflectance method) probe, which can accurately and precisely on-line monitor and control the temperature. The FBRM was applied to measure the solubility.[8,9] The apparatus was equipped with a 150 mL jacketed curved-bottom glass vessel, a downward glass propeller stirrer driven by a motor, a temperature sensor, and a thermostatic bath controlled by a PID controller with ± 0.1 K accuracy. It performed temperature control and monitoring in an automated and highly accurate mode. The temperature and number of particles were measured at 2 s intervals during the measurement of solubility.

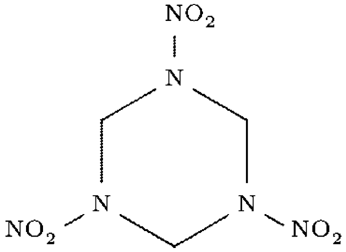

Figure 1. Chemical structure of RDX.

This method is based on sequentially adding known masses of solute to a stirred solution kept at a fixed temperature. Predetermined amounts of solute and solvent mixture of about 100.0 g were fed into the jacketed vessel. The amount of solvent was in small excess. After stirring at a fixed temperature for 1 h, an additional solute of known mass of about (0.008 to 0.01) g was fed into the vessel with continuous stirring. This procedure was repeated until the last addition of solute could not dissolve completely within the interval of addition of 30 min. Then, the total amount of the solute added (including the last addition) was used to compute the solubility. To prevent the evaporation of the solvent, a condenser was used. The masses of the samples and solvents were weighed using an analytical balance (Metler Toledo) with an uncertainty of 0.00001 g. The dissolution of the solute was monitored by the FBRM (Lasentec S400A). When the solute was dissolved completely, the solution was clear, and the particle was not detected. Some of the experiments were conducted in triplicate to check the reproducibility. The solubility for a given mixture was reproducible within ± 0.01 g of RDX/100 g of solution.

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Table 1. Mole Fraction Solubility and Activity Coefficient in Binary Solvents

γ-Butyrolactone + Water

	mass ratio of solvent (γ-butyrolactone(g) + water(g))							
T	1:0		5:1		3:1		1:1	
°C	x_1	γ	x_1	γ	x_1	γ	x_1	γ
20	0.0472	0.0728	0.0096	0.3578	0.0048	0.7123	0.0005	6.6101
40	0.0714	0.1228	0.0201	0.4351	0.0101	0.8712	0.0010	9.0108
60	0.1046	0.1906	0.0459	0.4342	0.0229	0.8698	0.0025	7.8990
80	0.1477	0.2800	0.0818	0.5055	0.0596	0.6934	0.0101	4.0933
90	0.1727	0.3346	0.1020	0.5668	0.0720	0.8025	0.0343	1.6836

Cyclohexanone + Water

	mass ratio of solvent (cyclohexanone(g) + water(g))							
T	1:0		5:1		3:1		1:1	
°C	x_1	γ	x_1	γ	x_1	γ	x_1	γ
20	0.0291	0.1182	0.0183	0.1881	0.0141	0.2442	0.0053	0.6456
40	0.0451	0.1943	0.0257	0.3405	0.0192	0.4561	0.0097	0.9072
60	0.0734	0.2715	0.0373	0.5345	0.0257	0.7772	0.0127	1.5726
80	0.0906	0.4563	0.0506	0.8173	0.0328	1.2605	0.0153	2.7052
90	0.1047	0.5520	0.0598	0.9671	0.0376	1.5358	0.0175	3.3026

N-Methyl Pyrrolidone + Water

	mass ratio of solvent (*N*-methyl pyrrolidone(g) + water(g))							
T	1:0		5:1		3:1		1:1	
°C	x_1	γ	x_1	γ	x_1	γ	x_1	γ
20	0.1611	0.0213	0.0237	0.1452	0.0082	0.4176	0.0002	19.8846
40	0.1885	0.0465	0.0398	0.2198	0.0152	0.5772	0.0005	17.6030
60	0.2201	0.0906	0.0642	0.3108	0.0320	0.6224	0.0023	8.7500
80	0.2581	0.1602	0.1039	0.3980	0.0615	0.6728	0.0062	6.7226
90	0.2794	0.2069	0.1308	0.4417	0.0877	0.6590	0.0122	4.7436

Acetone + Water

	mass ratio of solvent (acetone(g) + water(g))							
T	1:0		5:1		3:1		1:1	
°C	x_1	γ	x_1	γ	x_1	γ	x_1	γ
0	0.0129	0.0912	0.0048	0.2452	0.0029	0.4062	0.0003	3.8357
10	0.0152	0.1349	0.0063	0.3255	0.0038	0.3100	0.0005	2.3947
20	0.0193	0.1780	0.0088	0.3909	0.0049	0.6997	0.0007	5.1401
30	0.0234	0.2378	0.0112	0.4978	0.0064	0.8701	0.0009	5.8820
40	0.0259	0.3381	0.0133	0.6564	0.0077	1.1444	0.0014	6.1602

Results and Discussion

The solubilities of RDX in solvents were measured over the temperature range from 273 K to 363 K, and the values are listed in Table 1 and plotted in Figure 2. The solubilities of RDX increase with an increase in temperature and decrease with an increase in the water content.

It was found that exponential temperature dependence, as shown in Figure 2, permitted a linear interpolation. Thus, solubility of RDX with the temperature T was analyzed using the equation

$$x = a \exp[b(T/\mathrm{K})] \tag{1}$$

where x is the mole fraction solubility of RDX; T is the absolute temperature; and a and b are the parameters.

The linear expression describes satisfactorily the temperature dependence of the solubility, within the temperature range studied. The result shows that the equation can be used to correlate the solubility data of RDX in *N*-methyl pyrrolidone + water, cyclohexanone + water, butylolactone + water, and acetone + water. From the experimental data in Table 1, it can be seen that the solubility of RDX in *N*-methyl pyrrolidone is the highest and that solubility decreases with the increase of the content of water in the mixed solvent at constant temperature. The solubility of RDX in acetone is the lowest.

Table 2 presents parameters of a and b for eq 1 in binary solvent and the average absolute error, σ, of the correlation for each mixture. σ is defined as

$$\sigma = \frac{\sum_{i=1}^{N} \left| \frac{x_{\mathrm{exptl}} - x_{\mathrm{calcd}}}{x_{\mathrm{exptl}}} \right|}{N} \cdot 100 \tag{2}$$

where N is the number of experimental points. The subscripts calcd and exptl stand for the calculated values and the experimental values, respectively. The overall average absolute errors of each mixture are 3.8 %, 1.4 %, 4.3 %, and 1.1 % for γ-butyrolactone + water, cyclohexanone + water, *N*-methyl pyrrolidone + water, and acetone + water, respectively. It can be seen that eq 1 is satisfactory to correlate the experimental data.

The largest value of b was found in butylrolactone. The larger value of β means a higher dependence of the solubility on temperature. Thus, the cooling mode in crystallization is desirable in the solvents *N*-methyl pyrrolidone and butylrolactone. Solubility is very high in all solvents without water, in which the cooling mode is not desirable for crystallization but the evaporation and drowning-out modes are desirable. Solubility decreases very sharply with increasing water concentration. This means that the drowning-out mode is acceptable in binary solvents including water.

Data of solubility can be used to estimate the activity coefficient through the equilibrium relationship. The fundamental equation used to calculate the solid−liquid phase equilibria can be derived starting from the isofugacity criterion.[10] If no solid−solid transition occurs in the considered temperature range, with some useful simplifications it leads to the following formula which was described elsewhere[11]

$$\ln x_1\gamma_1 = \frac{-\Delta_{\mathrm{fus}}H_1}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m},1}}\right) \tag{3}$$

where x_1 is the mole fraction of component 1 (RDX) in the liquid phase; γ_1 is the activity coefficient of component 1 in the liquid phase; $\Delta_{\mathrm{fus}}H_1$ is the molar enthalpy of fusion of component 1; $T_{\mathrm{m},1}$ is the melting temperature of component 1; T is the absolute temperature of the mixture; and R is the gas constant. The melting point T_{m} and the enthalpy of fusion $\Delta_{\mathrm{fus}}H$ of RDX are 478.65 K and 35647.68 $\mathrm{J \cdot mol^{-1}}$, respectively.[1]

The activity coefficients γ_1 can be calculated using eq 3 from experimentally determined solution composition x and temperature T. Table 1 gives mole fractions, equilibrium temperatures, and activity coefficients according to the mass ratio of solvent to water. As can be seen in Table 1, in nearly all the cases, deviations from ideal solution are observed. The solubilities of RDX have a deviation from ideal values in the order: *N*-methyl pyrrolidone > γ-butyrolactone > cyclohexanone > acetone. Such deviations are attributed to the interaction of a chemical nature between the RDX and solvent.

To procure the enthalpy of dissolution of RDX crystals in solvent, eq 3 can be changed into eq 4, which is obtained from the ideal solution theory[10]

$$\ln x_1 = \frac{-\Delta_{\mathrm{sol}}H_1}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m},1}}\right) \tag{4}$$

where x_1 is the mole fraction of solute; $\Delta_{\mathrm{sol}}H_1$ is the enthalpy

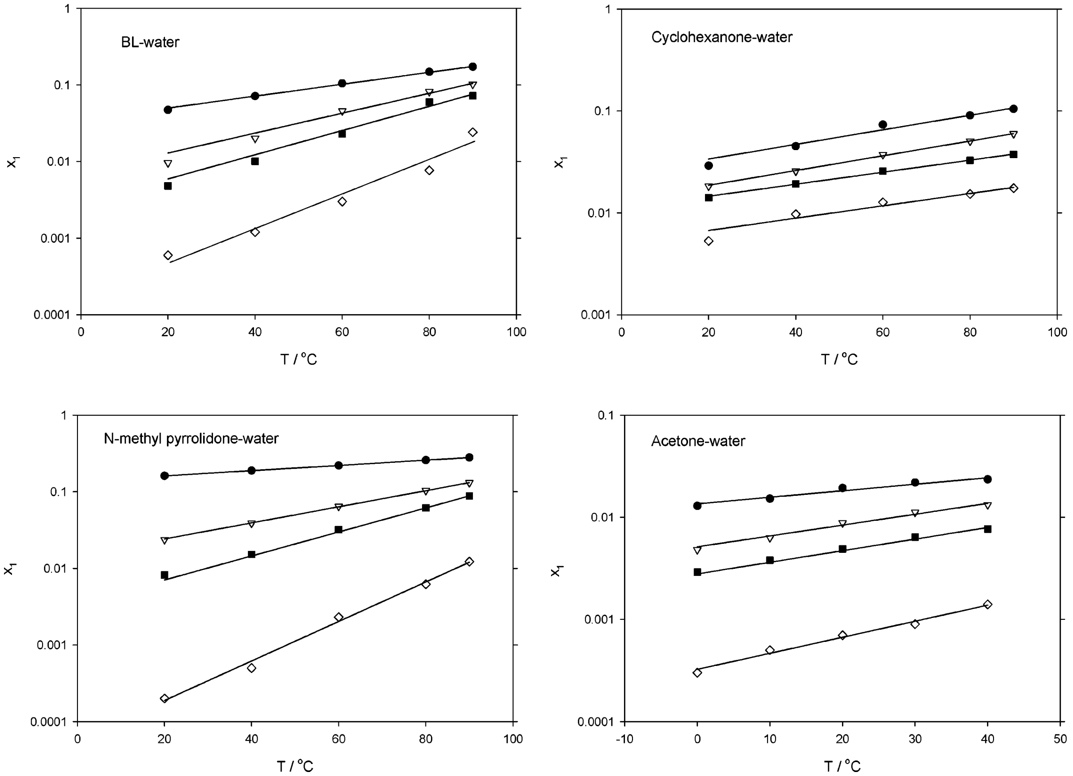

Figure 2. Mole fraction solubility, x, of RDX in the following solvents. γ-Butyrolactone(g) + water(g): •, 1:0; ▽, 5:1; ■, 3:1; ♦, 1:1. Cyclohexanone(g) + water(g): •, 1:0; ▽, 5:1; ■, 3:1; ♦, 1:1. *N*-Methyl pyrrolidone(g) + water(g): •, 1:0; ▽, 5:1; ■, 3:1; ♦, 1:1. Acetone(g) + water(g): •, 1:0; ▽, 5:1; ■, 3:1; ♦, 1:1. Lines are indicated by eq 1.

Table 2. Parameters *a* and *b* in Equation 1

solvent ratio	a/mole fraction	b/K^{-1}	σ
	γ-Butyrolactone + Water		
1:0	$2.65\cdot10^{-4}$	$1.79\cdot10^{-2}$	0.728
5:1	$2.02\cdot10^{-6}$	$2.99\cdot10^{-2}$	2.475
3:1	$1.40\cdot10^{-7}$	$3.64\cdot10^{-2}$	4.995
1:1	$3.24\cdot10^{-18}$	$1.02\cdot10^{-1}$	10.01
	Cyclohexanone + Water		
1:0	$2.71\cdot10^{-4}$	$1.65\cdot10^{-2}$	2.388
5:1	$1.41\cdot10^{-4}$	$1.67\cdot10^{-2}$	0.292
3:1	$2.71\cdot10^{-4}$	$1.36\cdot10^{-2}$	0.277
1:1	$1.14\cdot10^{-4}$	$1.39\cdot10^{-2}$	2.811
	N-Methyl Pyrrolidone + Water		
1:0	$1.60\cdot10^{-2}$	$7.87\cdot10^{-3}$	0.002
5:1	$2.19\cdot10^{-5}$	$2.40\cdot10^{-2}$	2.781
3:1	$3.47\cdot10^{-7}$	$3.43\cdot10^{-2}$	1.884
1:1	$2.38\cdot10^{-12}$	$6.16\cdot10^{-2}$	12.90
	Acetone + Water		
1:0	$1.10\cdot10^{-4}$	$1.75\cdot10^{-2}$	2.675
5:1	$6.43\cdot10^{-6}$	$2.45\cdot10^{-2}$	1.011
3:1	$4.45\cdot10^{-6}$	$2.39\cdot10^{-2}$	0.472
1:1	$1.67\cdot10^{-8}$	$3.62\cdot10^{-2}$	0.403

Table 3. Enthalpy of Dissolution and Enthalpy of Mixing

		$\Delta_{sol}H$	$\Delta_{mix}H$
solvent ratio	d(ln x)/d(T^{-1})	kJ·mol^{-1}	kJ·mol^{-1}
γ-Butyrolactone(g) + Water(g)	γ-Butyrolactone + Water Solvent		
1:0	−1975.3	16.4	−19.2
5:1	−3665.9	30.4	−5.16
3:1	−4271.6	35.5	−0.130
1:1	−6124.0	50.9	15.2
Cyclohexanone(g) + Water(g)	Cyclohexanone + Water Solvent		
1:0	−1960.3	16.2	−19.3
5:1	−1805.7	15.0	−20.6
3:1	−1485.2	12.3	−23.2
1:1	−1719.8	14.3	−21.3
N-Methyl Pyrrolidone(g) + Water(g)	*N*-Methyl Pyrrolidone + Water Solvent		
1:0	−836.3	6.9	−28.6
5:1	−2592.7	21.5	−14.0
3:1	−3618.4	30.0	−5.56
1:1	−6517.2	54.1	18.5
Acetone(g) + Water(g)	Acetone + Water Solvent		
1:0	−1565.2	13.0	−22.6
5:1	−2244.3	18.6	−16.9
3:1	−2107.8	17.5	−18.1
1:1	−3180.1	26.4	−9.20

of dissolution of RDX; and T_m is the melting temperature of RDX. $\Delta_{sol}H_1$ is equal to $\Delta_{fus}H_1$ for an ideal system, which is obtained by taking $\gamma_1 = 1$ in eq 3 and $\Delta_{fus}H_1 + \Delta_{mix}H_1$ for nonideal systems.

The enthalpy of mixing, $\Delta_{mix}H_1$, is a measure for the solute−solvent interaction, whereas the enthalpy of fusion $\Delta_{fus}H_1$ is solvent independent. Through the plot of ln x_1 vs T^{-1}, the enthalpy of dissolution was calculated using its slope, d ln x_1/dT^{-1}, and its values are listed in Table 3. The heat of dissolution of RDX in all solvents studied was exothermic.

In the case of solvent without water, it was found that $\Delta_{mix}H_1$ increases in the order: *N*-methyl pyrrolidone > acetone > cyclohexanone > γ-butyrolactone. Such a large $\Delta_{mix}H_1$ shows a large solvent−solute interaction, and this could have a large effect on the inclusion of solvent inside the crystals, which generates the defect inside the crystals. It supports the previous results that the crystals obtained in solvent γ-butyrolactone have less defects than those obtained in solvent acetone.[3,4] $\Delta_{mix}H_1$ depends on the water content in the solvent. This supports that defects of RDX crystals prepared in solvent cyclohexanone + water were decreased, compared to that in solvent cyclohexanone.[1,3,4]

The enthalpies of dissolution of RDX depend on solvent composition. In the case of cyclohexanone, there is little variation of the enthalpy of dissolution with the concentration of water, although the scatter of data may mask any effects that are smaller than about 3 kJ·mol^{-1}.

Deviations from such behavior are seen as positive enthalpies of mixing, which drive the solution toward immiscibility (e.g., in increasing the content of water in binary solvents) or negative enthalpies of mixing (homogeneous single liquid). Energetically ideal behavior could imply thermal mixing of different component structural units derived from solvents and nonsolvent components. However, the enthalpy of dissolution of RDX in all solvents is very exothermic and indicates an energetically favorable mixing between RDX and solvent.

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