Solubility of RDX in Dense Carbon Dioxide at Temperatures between 303 K and 353 K

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The solubility of the high-explosive cyclotrimethylenetrinitramine (RDX) in carbon dioxide (CO_2) is measured over a temperature and pressure range of 303 K to 353 K and 6.9 MPa to 48.3 MPa, respectively. A high-pressure ultraviolet chromatographic detector is used to measure in situ solute levels of RDX in a dynamic flow apparatus. RDX is found to be relatively insoluble in CO_2, with a maximum solubility of about 0.25 mg/g CO_2 at the highest temperatures and pressures studied. Empirical fits of the solubility isotherms are determined as a function of the solvent density and solute vapor pressure. The spectroscopy of RDX is also examined as a function of CO_2 temperature and pressure to confirm the suitability of the method for determination of solubility.

Introduction

The use of nondestructive supercritical fluid technologies for the analysis (Ashraf-Khorassani and Taylor, 1989a,b; Griest et al., 1989; Via and Taylor, 1992; Martinez et al., 1995), processing (Gallagher et al., 1989; McHugh and Krukonis, 1994), and demilitarization (Melvin, 1990) of energetic materials has been under investigation for the past decade. One energetic material of particular interest to the military is cyclotrimethylenetrinitramine, more commonly known as RDX. Millions of kilograms of RDX can be found in military explosives formulations in the demilitarization stockpiles of the U.S. Department of Defense. It is clear that environmental concerns over formerly acceptable demilitarization techniques, such as open burning and open detonation, will severely limit their future use. One can expect that laws such as the Resource Conservation and Recovery Act, which already apply to many commonly used goods, will eventually require the recovery and recycling of at least some of the energetic ingredients found in military propellants and explosives. With bulk RDX prices in the range of $10/kg and greater, sufficient economic incentive should exist for the recovery, rather than destruction, of this material.

Supercritical fluid extraction (SFE) is one approach under consideration in our laboratory for the separation and recovery of nitramine energetic materials, such as RDX, from energetic formulations. One possibility under consideration is the direct extraction of RDX from the propellant or explosive. However, many energetic formulations consist of greater than 50% RDX. In these cases, it may make more economic sense to extract the secondary ingredients, such as stabilizers, plasticizers, and certain binder ingredients. While mass transfer or diffusion limitations can have a large influence on an extraction process, it is clear that the solubilities of all the chemical components involved in the formulation need to be considered for solvent selection and process design.

The objective of the present work is to quantify the solubility characteristics of RDX in CO_2 as a function of temperature and pressure. Carbon dioxide is relatively cheap (8¢/kg in bulk) and has relatively little environmental impact. While CO_2 is a greenhouse gas, large-scale SFE plants can be run using closed-loop designs to minimize gas emissions. It is clear that the use of environmentally benign processing solvents, such as CO_2, will play an increasingly important future role in complying with environmental regulations for both the manufacture and demilitarization of energetic materials.

Experimental Section

The apparatus used to determine the solubility of RDX in dense CO_2 is shown schematically in Figure 1. A 260-mL syringe pump (ISCO) is filled with liquid CO_2. An analytical-scale SFE unit is configured with the extraction vessel in a sample injection loop in line with the CO_2 flow from the syringe pump. The extraction vessel consists of a 2-in. length of thick-walled 0.25-in.-diameter stainless steel tube equipped with fritted end fittings; the bore of the tube is 0.12 in. The internal volume of the vessel is approximately 0.5 mL. The extraction vessel is placed in an aluminum heating block inside the extraction unit, which is resistively heated to the desired operating temperature. A liquid chromatographic multiwavelength ultraviolet−visible (UV−vis) detector (Thermo Separation Products), equipped with a high-pressure 250-nL flow cell, is used to detect solute levels in the fluid. The flow cell and the transfer line from the extraction unit are thermally stabilized using a thermostated water circulator (not shown in Figure 1). A variable linear restrictor (ISCO) is used to adjust the CO_2 flow rate through the system. The CO_2 expands to an ambient pressure of 0.1 MPa as it exits the flow restrictor, and the nucleated solute is collected in acetonitrile (99.98%, EM Science). All transfer lines between the equipment shown in Figure 1 consist of 1/16-in. stainless steel tubing. The maximum operating pressure of the apparatus is determined by a pressure limitation of 48.3 MPa for the flow cell on the UV−vis detector.

Dynamic solubility measurements are carried out in SFC grade CO_2 (99.99%, Matheson Gas Products). Efficient fluid transfer from the cylinder to the syringe pump is achieved without the use of a helium headspace by chilling the pump to subambient temperature. The pump cylinder is equipped with a water jacket; circulation of cold tap water through this water jacket is sufficient to cool the pump.

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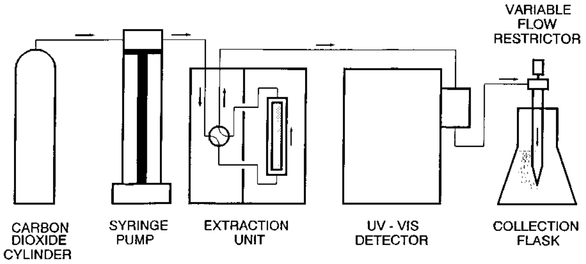

Figure 1. Block schematic of the apparatus used for measurement of RDX solubility in supercritical CO_2.

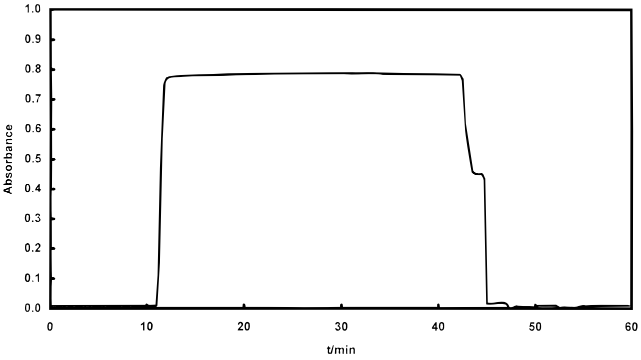

Figure 2. Typical RDX solubility profile in CO_2 with UV detection at 246 nm. The extraction vessel is put on-line at 10 min and is taken off-line at 40 min.

The RDX is recrystallized twice using acetone (99.5%, Alltech). The main impurity found in RDX is cyclotetramethylenetetranitramine, or HMX. On the basis of high-performance liquid chromatographic (HPLC) analysis, the recrystallized RDX is found to contain substantially less than 1% HMX. Small quantities of the RDX are ground using a mortar and pestle. The ground RDX is sieved through a 100-mesh (150-μm) screen tray (W. S. Tyler). The extraction vessel is filled with the fine crystalline RDX, and the RDX is pre-extracted with supercritical CO_2 to remove residual acetone. If the acetone is not removed, initial solubility runs can result in misleading measurements that are too high due to an acetone cosolvent effect. HPLC analyses performed on some of the acetonitrile solutions collected following the RDX solubility runs indicate extraction of no detectable HMX from the RDX samples.

Safety note: RDX is an extremely energetic material. Utmost care is taken when reducing the RDX particle size. Particular caution is required when sealing the extraction vessel to ensure that no RDX is trapped between the threads of the vessel cap.

A typical RDX solubility profile is shown in Figure 2. The detector wavelength is set to 246 nm for the solubility measurements. A UV absorbance baseline is established by collecting data while bypassing the extraction vessel, allowing solute-free CO_2 to flow through the detector. After 10 min, the extraction vessel is put on-line, allowing the CO_2 to saturate with RDX. Equilibration typically occurs within several minutes, and the vessel is kept on-line for 30 min. The variable restrictor is adjusted to keep the flow rate of liquid CO_2, measured at the pump, around 0.5 mL/min or less. The actual flow of supercritical CO_2 through the extraction vessel is somewhat higher, as determined by the ratio of CO_2 density in the liquid and supercritical states at the same pressure but different temperatures.

Referring to Figure 1, the UV−vis detector is calibrated as follows. The extraction unit and variable flow restrictor are removed, and a transfer line with a 2-mL sample injection loop is connected between the syringe pump and the flow cell on the UV−vis detector. The detector is put into rapid scanning mode over a range of 200−400 nm, with a 1-nm resolution. The syringe pump is filled with acetonitrile and is set to a constant flow rate of 0.5 mL/min. The sample injection loop is filled with calibration solutions of RDX in acetonitrile. The sample loop is brought on-line, and spectra of each calibration solution are recorded. Spectra from the three most dilute calibration solutions (20 mg/L to 80 mg/L) of RDX in acetonitrile are averaged. The original experimental setup is restored, and seven spectra of RDX in supercritical CO_2 are recorded over a range of detector flow cell temperatures of 308 K to 353 K and pressures of 20 MPa to 50 MPa. The seven RDX spectra measured in supercritical CO_2 are averaged for comparison with the averaged spectra measured in acetonitrile. The averaged spectra, normalized to the peak maximum of the lowest energy RDX UV transition, are shown in Figure 3. A reasonable match is observed between the averaged spectra of RDX in supercritical CO_2 and an 8-nm blue-shift of the averaged spectra of RDX in acetonitrile in the range of 220 nm to 300 nm. The solubility profiles for RDX in CO_2, measured at 246 nm, are calibrated using a Beer−Lambert plot of the RDX absorbance in acetonitrile at 254 nm.

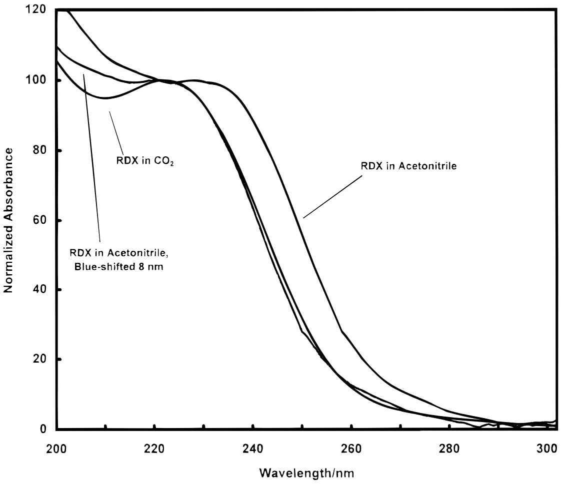

Figure 3. Normalized and averaged spectra of RDX in CO_2 and acetonitrile.

The net RDX absorbance at 246 nm for each solubility run is determined by subtracting the average baseline absorbance of solute-free CO_2 from the average absorbance of CO_2 that is saturated with RDX after the system has equilibrated. Mass solubilities (mg of RDX/g of CO_2) and RDX mole fractions are determined from the UV−vis detector calibration and the CO_2 density.

Results and Discussion

Solubility isotherms for RDX in CO_2 are measured at 303 K, 308 K, 323 K, 338 K, and 353 K, across a pressure range of 6.9 MPa to 48.3 MPa. Table 1 lists the solubility of RDX in CO_2 at these temperatures and pressures. The mass solubilities listed in Table 1 are converted into mole fractions and plotted as solubility isotherms in Figure 4. For the majority of the data, a single measurement is made at each set of temperature and pressure conditions. In cases where multiple measurements are made at a given set of temperature and pressure, the results are averaged. The maximum RDX mass solubility in CO_2 measured in these experiments is about 0.25 mg of RDX/g of CO_2. The

Table 1. Mass Solubility of RDX in CO_2 (mg of RDX/g of CO_2) as a Function of Temperature and Pressure

	solubility				
P/MPa	303 K	308 K	323 K	338 K	353 K
6.9	0.002	0.000	0.000		
10.3	0.007	0.008	0.003	0.001	
13.8	0.013	0.013	0.013	0.009	0.004
27.6	0.032	0.034	0.051	0.076	0.114
41.4	0.053	0.067	0.097[a]	0.173	0.237[b]
48.3	0.055	0.064	0.111	0.173	0.254[b]

[a] Average of seven measurements. [b] Average of two measurements.

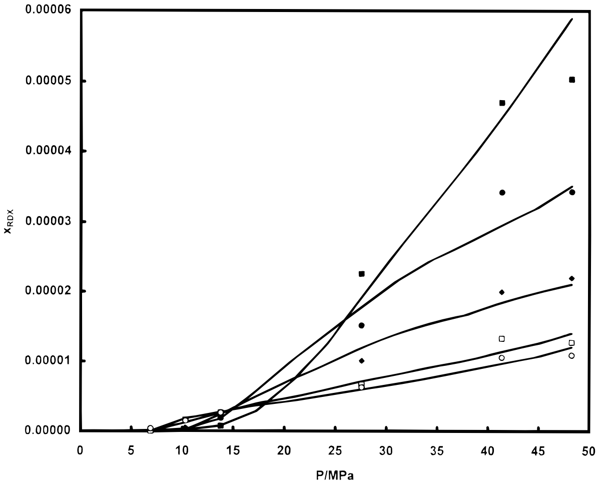

Figure 4. RDX solubility isotherms in CO_2: (■) 353 K; (●) 338 K; (◆) 323 K; (□) 308 K; (○) 303 K; (—) eq 3.

permanent dipole moment for RDX has been determined through ab initio Hartree−Fock self-consistent field calculations to be 6.5 D (Zahner, 1995). The fact that RDX is even sparingly soluble in CO_2 can be attributed to the relatively large CO_2 quadrupole moment that results from its π bonding structure, and the dipole−quadrupole potential energy interaction between RDX and CO_2.

Rice et al. (1995) raise an important consideration regarding absorbance-based solubility determinations in their paper on density-dependent changes in solute molar absorptivities in supercritical CO_2. In the cases of anthracene and pyrene dissolved in CO_2, they report significant variations in the magnitude of the molar absorptivity as well as substantial red-shifts in the UV spectra of these solutes as the reduced density of the fluid is increased from 0.714 to 1.91. The implication is that these density-based spectral shifts and variations in molar absorptivity can create a substantial bias in any single, fixed wavelength solubility determination.

The potential for such bias is investigated in the case of RDX. Table 2 presents the spectroscopic parameters for the seven individual spectra of RDX in CO_2 that are normalized and averaged for use in the detector calibration. RDX is dissolved in CO_2 at a temperature of 308 K for all seven spectra. Density effects are probed by varying the detector temperature. The values listed in Table 2 include the pressure, the detector temperature, the peak maximum for the lowest energy UV transition, the measured absorbance at the peak maximum, the ratio of the absorbance at the peak maximum to that at 246 nm, the CO_2 reduced density, and the ratio of absorbance at the peak maximum to reduced density. It is immediately apparent that no substantial shifting of the peak maximum is observed for RDX in the CO_2 reduced density range of 1.29 to 2.10. The ratio of the absorbance at the peak maximum to that at 246 nm shows only random fluctuations over the ranges of temperature and pressure examined, displaying a relative standard deviation of about 4%.

The lack of substantial density-dependent red-shifting of the UV spectrum of RDX, such as that seen in the cases of anthracene and pyrene (Rice et al. 1995), warrants further consideration. In the case of RDX, the lowest energy UV absorption is most likely due to an $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ electronic transition. In the cases of pyrene and anthracene, which are highly conjugated aromatic hydrocarbons, the lowest energy UV absorption bands must correspond to $\pi \rightarrow \pi^*$ electronic transitions. The delocalized π and π^* orbital systems in these large aromatic molecules are expected to be much more diffuse and polarizable than the atomic nonbonding orbitals and π^* orbitals localized to the NO_2 groups in RDX. For electronic transitions involving solutes dissolved in supercritical fluids, features such as density-dependent spectral shifting appear to be strongly affected by the nature of the molecular orbitals involved in the transitions. In light of these considerations, the insensitivity of the spectroscopic features of RDX relative to changes in the solvent density is not surprising.

The data listed in Table 2 can also be used to get an idea of the magnitude of the variation of molar absorptivity as a function of temperature under isobaric conditions. Since all of the RDX is dissolved at a temperature of 308 K, both spectra measured at a pressure of 20.7 MPa should have the same mass of solute per gram of CO_2. The same should also apply to the three spectra measured at a pressure of 41.4 MPa. The absorbance measured at the peak maximum is proportional to the mass of RDX in the 250-nL microflow cell volume. When the detector temperature is raised, the fluid density decreases. The resulting fluid volume expansion results in decreases of the observed absorbance, which is due to a volumetric dilution of the mass of RDX in the flow cell. Absorbance decreases are observed in both sets of data in Table 2, at 20.7 MPa and again at 41.4 MPa, as the temperature is raised. To put these measurements on a constant mass basis, the absorbance at the peak maximum is divided by the reduced density. When this is done, a difference of about 30% is noted between the two measurements at 20.7 MPa. The spread is substantially smaller at 41.4 MPa, with a relative standard deviation of about 5%.

Ideally, one would like to fit solubility data such as that listed in Figure 4 to a cubic equation like the Peng−Robinson equation of state (McHugh and Krukonis, 1994). To carry out solubility modeling, one needs to know a fair amount of molecular property information for both the solvent and solute molecules. Most of the required information is unavailable for RDX. While several group additivity methods are known for the estimation of critical parameters, these techniques generally require the knowledge of a boiling point (Reid et al., 1987). RDX is known to thermally decompose upon melting at 478 K (Adams and Shaw, 1992). Group contributions are generally not available for nitramine ($N-NO_2$) functionalities. It is questionable whether meaningful estimates for the critical pressure, critical temperature, and acentric factor—all of which are required for equation of state modeling—can be obtained for RDX using group contribution techniques.

Bartle et al. (1991) review a technique to fit supercritical CO_2 solubility data to the following equations

$$\ln(E) = a + b\rho \tag{1}$$

Table 2. Parameters for Spectra of RDX Dissolved in CO_2

P/MPa	detector temp/K	peak max/nm	abs. at peak max/maU	(abs. at peak max)/(abs. at 246 nm)	reduced density	(abs. at peak max)/(reduced density)
20.7	308	222	148	2.24	1.88	78.7
20.7	353	222	133	2.33	1.29	103
27.6	353	222	199	2.43	1.54	129
41.4	308	223	370	2.19	2.10	176
41.4	338	222	366	2.26	1.89	194
41.4	353	222	324	2.26	1.78	182
48.3	353	222	457	2.13	1.86	246

$$E = xP/P_{\text{vap}} \tag{2}$$

where a and b are empirically determined fitting parameters, ρ is the system density, x is the solute mole fraction, P is the system pressure, and P_{vap} is the solute vapor pressure. The quantity E, defined in eq 2, represents the enhancement of solute concentration in the supercritical phase relative to the concentration based on a partial pressure equal to the solute vapor pressure at a total system pressure of 0.1 MPa. For dilute solutions, the density of CO_2 can be used to approximate ρ. Since P_{vap} and ρ are both temperature-dependent quantities, eqs 1 and 2 are used to make isothermal fits to the solubility data. The fitting parameters are obtained by calculating E for each condition of temperature and pressure and performing a linear regression on eq 1 at isothermal conditions. The data at the two lowest pressures are omitted from the linear regression analysis for reasons discussed by Bartle et al. (1991), resulting in a four-point fit for each isotherm. A representative plot of ln(E) versus CO_2 density, which shows the linear relationship between solubility and density, is shown in Figure 5. In cases where multiple measurements are made at a given set of temperature and pressure conditions, the data are averaged so as not to impart undue weight to that point in the regression analysis. The RDX vapor pressure data of Dionne et al. (1986) used to make these fits are listed in Table 3, along with the empirically determined values for the fitting parameters. Carbon dioxide density values are obtained using the commercial ISCO computer program SF-Solver. Equations 1 and 2 can be solved in terms of the solute mole fraction:

$$x = (P_{\text{vap}}/P)\exp(a + b\rho) \tag{3}$$

The density-dependent fits to the RDX solubility data are plotted as isotherms in Figure 4.

Equilibration of the solubility measurement is checked at 323 K and 41.4 MPa by repeating the solubility measurement at seven different CO_2 flow rates. The solubility measurements are found to be subject only to random variations for flow rates in the range of 0.2 mL/min to 1.8 mL/min at 323 K and 41.4 MPa, indicating the supercritical fluid is saturated with solute at these conditions. If the fluid were not saturated with solute at the higher flow rates, an increase in solute concentration would have been observed at the lower flow rates, due to the longer contact time of the fluid with the RDX in the extraction vessel. At these temperature and pressure conditions, the seven solubility measurements made to check for solubility equilibration can also be used to get an idea of the error estimate for these experimental measurements. The solubility is determined to be 0.097 (±0.009) mg of RDX/g of CO_2 at 323 K and 41.4 MPa.

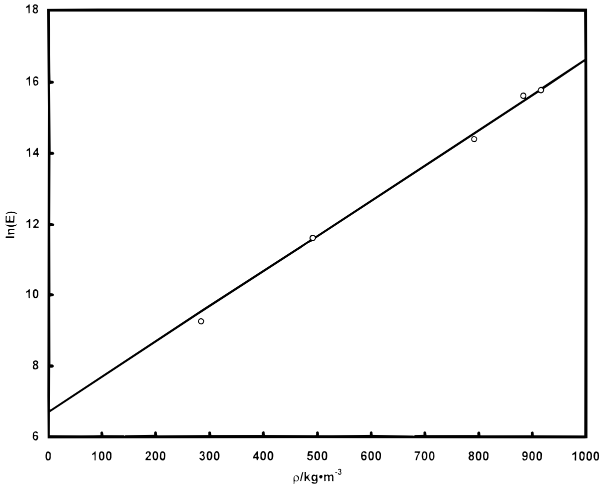

Figure 5. Plot of ln(E) versus CO_2 density at 338 K. Fitting parameters a and b listed in Table 3 are determined from the intercept and slope, respectively, of the line resulting from linear regression analysis of the data points.

Table 3. RDX Vapor Pressure[a] (P_{vap}) and Fitting Parameters (a, b) for RDX Solubility Isotherms in CO_2

T/K	P_{vap}/MPa	a	b/m^3·kg^{-1}
303	1.42×10^{-12}	3.976	0.015 45
308	3.16×10^{-12}	4.509	0.014 52
323	2.98×10^{-11}	6.003	0.011 63
338	2.31×10^{-10}	6.705	0.009 94
353	1.50×10^{-9}	4.701	0.011 22

[a] See Dionne et al. 1986.

The form of the solubility isotherms shown in Figure 4 is typical of most organic compounds. Solubility isotherms for almost 90 low-volatility substances can be found in Bartle et al. (1991). Retrograde solubility behavior exhibited at pressures less than about 15 MPa for RDX is also observed in a large number of organic solute/CO_2 systems at relatively low pressures and is attributed to the large variation in CO_2 density as a function of temperature under isobaric conditions at these pressures.

Conclusions

RDX is found to display limited solubility in CO_2. The solubility of RDX in this system is found to vary by more than 2 orders of magnitude over a range of temperature and pressure up to 353 K and 48.3 MPa, with a maximum solubility of about 0.25 mg of RDX/g of CO_2.

Analysis of the spectral features of RDX in CO_2 under various temperature and pressure conditions reveals no substantial shifting of the spectra as a function of fluid density. However, substantial density-dependent redshifting has been reported by Rice et al. (1995) for anthracene and pyrene in supercritical CO_2. For in situ spectroscopic determinations of solubility in supercritical fluids, the suitability of the method needs to be checked against the spectroscopy of the solute molecule on a case-by-case basis.

Given the limited solubility of RDX, it will probably not be practical to consider direct extraction of RDX from an energetic formulation using unmodified CO_2. However, SFE of RDX-based formulations may be a useful approach for the separation and removal of the more extractable ingredients.

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