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Solubility and Phase Behavior of CL20 in Supercritical Fluids

Veera Boddu, Rebecca K. Toghiani,
and Reddy Damavarapu

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Veera M. Boddu

*Construction Engineering Research Laboratory
U.S. Army Engineer Research and Development Center
PO Box 9005
Champaign, IL 61826-9005*

Rebecca K. Toghiani

*Dave C. Swalm School of Chemical Engineering
Mississippi State University
Mississippi State, MS 39762*

Reddy Damavarapu

*Energetic & Warheads Division
U.S. Army Armament Research, Development and Engineering Center
Picatinny Arsenal, NJ 07806-5000*

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Abstract: The solubility of CL20 in supercritical carbon dioxide (CO₂) was evaluated using the Peng-Robinson cubic equation of state. Thermodynamic properties of CL20 were required for this estimation. A comprehensive search of the literature revealed little data regarding the critical point of the compound. Also lacking were vapor pressure data for the compound. Critical properties as well as other required thermodynamic properties were estimated using a variety of available estimation techniques, including the group contribution methods of Lydersen and of Joback. The solubility of CL20 in supercritical CO₂ was estimated using a Fortran program developed during the course of this project. Estimations spanned a reduced temperature range of 1.003 to 1.21 and a reduced pressure range of 1.01 to 2.06 with respect to carbon dioxide. The Fortran program was validated using available literature data for the solubility of naphthalene and of biphenyl in supercritical CO₂. The applicability of the estimation techniques employed for the critical properties for CL20 was established using these same techniques to estimate the critical properties of comparable compounds, including RDX and HMX. Solubility data for RDX in supercritical CO₂ reported in the literature were also used to establish the validity of the estimation approach.

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Preface

This study was conducted for the U.S. Army Armament Research, Development and Engineering Center (ARDEC), Picatinny Arsenal, NJ under customer order MIPR3EPIC0057; work unit CNE-L215H4, “Evaluate supercritical fluids for solventless (green) granulation of the explosive CL20.” The technical monitor was Dr. Reddy Damavarapu, Picatinny Arsenal, AMSRD-ARR-AEE-E.

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The CERL Principal Investigator was Dr. Veera Mallu Boddu. Part of this work was done by Dr. Rebecca K. Toghiani, Swalm School of Chemical Engineering, Mississippi State University under DACA42-03-P-0352. Deborah Curtin is Acting Chief, CN-E, and Dr. John T. Bandy is Chief, CN. The associated Technical Director is William D. Goran. The Director of CERL is Dr. Ilker Adiguzel.

CERL is an element of the U.S. Army Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Commander and Executive Director of ERDC is COL Richard B. Jenkins, and the Director of ERDC is Dr. James R. Houston.

Unit Conversion Factors

Multiply	By	To Obtain
atmosphere (standard)	101.325	kilopascals
bars	100	kilopascals

1 Introduction

Background

CL20, a high-energy explosive compound, is a polyazapolycyclic caged polynitramine (2,4,6,8,10,12-Hexanitro- 2,4,5,8,10,12-hexaazaisowurtzitane). Of the several crystalline phases of CL20, the ϵ -CL20 has highest density (2.044 g/cm³) and thermal stability (Nielson et al. 1998). The combustion and detonation characteristics of the CL20 can be improved if it is formed into nanoparticles of uniform size. Conventional methods to form ultrafine particles with narrow size distributions generally follow either size reduction or comminution by direct generation routes such as dispersion reactions, spray drying, or controlled recrystallization. Most of these processes are energy intensive, generate hazardous waste streams, and result in particles with wide size distribution and shapes. A new promising process using environmentally benign compressed gases as either solvents or anti-solvents is being investigated for applications in pharmaceutical and other industries. This process shows that ultrafine particles can be developed using supercritical fluids (SCF) without generating large quantities of solvent wastes. This process may be termed as a green manufacturing process for producing nanocrystalline particles of ϵ -CL20. Information on various aspects of fluid dynamics, thermodynamics, and mass transfer including nucleation and atomization, crystal growth, and agglomeration of CL20 in supercritical carbon dioxide (CO₂) are required to develop such a process. This project was focused to develop a model for prediction of solubility of CL20 in supercritical CO₂.

The solubility of CL20 in supercritical CO₂ must be estimated to determine the feasibility of using supercritical processing for production of explosive grade CL20. The solubility of a solute in a supercritical fluid can be readily evaluated using an equation of state, but necessary thermodynamic information required for the evaluation must be either available in the literature or predicted using available techniques. The approach taken in this work was to ascertain what data were available in the literature for the compound of interest and for other similar energetic compounds. The validity of available estimation techniques for the required thermodynamic properties was then assessed through comparison of the predictions with literature data where available.

Objective

The specific objective of the research was to develop a thermodynamic model to obtain solubility of ϵ -CL20 in supercritical CO₂. The model thus developed shall be validated with available experimental solubility of similar nitroaromatic explosives in supercritical CO₂.

Approach

To obtain solubility of the CL20 in supercritical CO₂ and solutions of CO₂ and co-solvents selected, based upon prior experience of ARDEC and literature information, involves estimating critical properties (from literature or use group contribution methods), and thermophysical and transport properties of the compounds involved. The phase behavior of the system was modeled in FORTRAN computer language with a cubic equation of state such as Peng-Robinson Equation of State (Peng and Robinson 1976) or any such equation of state. The solubility data obtained in the literature were used to obtain interaction parameters of the equation of state.

Mode of Technology Transfer

Information contained in this report can be used as a basis for developing green processes to produce high density particulate explosives. The results of this research help in reducing waste streams generated during the manufacturing processes. The results of this research will be made available to the Armament Research and Development Center (ARDEC) and to the Pollution Prevention and Environmental Quality Technology (EQT) Programs. Results of this research are also presented at the 24th Army Science Conference.

This report will be accessible through the World Wide Web (WWW) URL:
<http://www.cecer.army.mil>

2 Literature Review

A comprehensive review of the literature was conducted to identify sources of thermodynamic information for CL20 and similar energetic compounds including cyclotrimethylene-trinitramine (RDX) and cyclotetramethylene-tetranitramine (HMX). These other energetic compounds were included since they have been used as explosive agents for a longer time, so more information was likely to be available. The available data for these compounds could then be used to validate estimation techniques for the thermodynamic properties of CL20. Two computerized searches were conducted and yielded different items of interest.

Beilstein Database

Available information on the compounds of interest was compiled through use of the Chemical Abstracts Service (CAS) registry numbers (CL20, CAS# 135285-90-4; RDX, CAS# 121-82-4; HMX, CAS# 2691-41-0). Of particular interest was the determination of what data were available in the literature, including: the critical point (temperature, pressure, volume, compressibility), the melting point, the acentric factor, the latent heat of vaporization, vapor pressure, and liquid and/or solid density. For CL20, the only relevant data contained in the database were crystal density (solid density) and melting point. No references were reported associated with the critical point, the normal boiling point, or phase change properties (latent heat, vapor pressure). For RDX, relevant references were found for the critical temperature, critical volume, vapor pressure, and melting point. The values obtained from the references are compiled in Table 1.

For HMX, relevant references were also identified for these properties, excepting vapor pressure. The values obtained from the references are compiled in Table 2.

Table 1. Thermodynamic information for RDX (compiled from Beilstein Search).

Property	Value	Reference
Critical Temperature	567 °C	Maksimov (1992)
Critical Volume	442000 cm ³ /gmol	Maksimov (1992)
Vapor Pressure	0.000036–0.0004 mm Hg @ 110.6–138.5 °C	Edwards (1953)
Melting Point	Range: 272 to 278 °C	Burov et al. (1999)

Table 2. Thermodynamic information for HMX (compiled from Beilstein Search).

Property	Value	Reference
Critical Temperature	654 °C	Maksimov (1992)
Critical Volume	611000 cm ³ /gmol	Maksimov (1992)
Enthalpy of Vaporization	158599.97 J/mol @ 234 °C	Behrens (1990)
Melting Point	Range: 198 to 205°C	Suri and Chapman (1988) Burov et al. (1999)

Chemical Abstracts Database

The Chemical Abstracts Database revealed additional information for the compounds of interest. For RDX, two items of significance were identified. Dionne et al. (1986) measured the vapor pressure of RDX as a function of temperature over the temperature range 37 to 102 °C. Morris (1998) measured the solubility of RDX in dense CO₂ over the temperature range of 303 to 353 K. These data provide a means to assess the validity of the approach taken to estimate vapor pressure and to predict the solubility in supercritical CO₂ for the compound of interest. The majority of other citations obtained through this search, while of interest, were not relevant to the tasks involved in this work.

3 Evaluation of Solubility in a Supercritical Fluid

The basis for predicting the solubility of a solute in a supercritical fluid solvent is the equivalence of fugacities for the particular solute in each phase:

$$\hat{f}_i^s = \hat{f}_i^f \quad (\text{Eq 1})$$

where the superscript s represents the solid phase and f the supercritical fluid phase. If the solubility of the supercritical fluid in the solid phase is assumed negligible, then the fugacity of the solute in the solid phase, $\hat{f}_i^s$, is equal to the fugacity of the pure solute, f_i^s . The fugacity of the pure solute in the solute phase is evaluated using (Sandler 1989):

$$f_i^s = P_i^{\text{sat}} \left(\frac{f_i^{\text{sat}}}{P} \right) \exp \left[\int_{P_i^{\text{sat}}}^P \left(\frac{V_i^s}{RT} \right) dP \right] \quad (\text{Eq 2})$$

The molar volume of the pure solute, V_i^s , is assumed constant. The fugacity of the pure solute in the saturated state, f_i^{sat} , is combined with the pressure in the denominator to form the fugacity coefficient of the pure solute in the saturated state, ϕ_i^{sat} . Integration of Equation 2 with these substitutions yields (Sandler 1989):

$$f_i^s = P_i^{\text{sat}} \phi_i^{\text{sat}} \exp \left[\frac{V_i^s}{RT} (P - P_i^{\text{sat}}) \right] \quad (\text{Eq 3})$$

For many low volatility compounds, the fugacity coefficient for the pure solute in the saturated state is very nearly unity due to the extremely low vapor pressure of these compounds at ambient conditions.

The fugacity of the solute in the supercritical fluid phase is given by:

$$\hat{f}_i^f = y_i \hat{\phi}_i P \quad (\text{Eq 4})$$

where y_i is the mole fraction of solute in the supercritical fluid phase, also defined as the solubility of the solute in the supercritical fluid; $\hat{\phi}_i$ is the fugacity

coefficient for the solute in the supercritical fluid phase; and P is the system pressure.

Combination of Equations 3 and 4 yields an expression for the solubility of the solute, y_i , in the supercritical fluid (Sandler 1989):

$$y_i = \left(\frac{P_i^{\text{sat}}}{P} \right) \left(\frac{1}{\hat{\phi}_i} \right) \exp \left[\frac{V_i^s (P - P_i^{\text{sat}})}{RT} \right] \quad (\text{Eq 5})$$

The ideal solubility of the solute, a function of temperature and pressure, is represented by the first bracketed term in the expression. For the compounds of interest, the ideal solubility will be extremely low due to the low vapor pressure of the solute and the high pressure required to achieve supercritical conditions. Non-ideal behavior of the supercritical fluid phase is represented by the second bracketed term in the expression. The last term is the Poynting factor, which represents the effect of pressure on the solid phase. The last two bracketed terms, when combined, are known as the enhancement factor. This factor represents the increase in solubility due to the solvent's supercritical state.

The fugacity of the solute in the supercritical fluid can be evaluated using a cubic equation of state such as the Redlich-Kwong-Soave or the Peng Robinson equations. The Peng-Robinson equation is used in this work. The Peng-Robinson equation for a mixture is (Modell and Reid 1983):

$$P = \frac{RT}{V - b_M} - \frac{a_M}{V(V + b_M) + b_M(V - b_M)} \quad (\text{Eq 6})$$

where V is the molar volume of the mixture while a_M and b_M are mixture-dependent parameters. For the Peng-Robinson equation of state, these mixture parameters are evaluated from mixing rules where the pure component analogues, calculated from the critical properties, the acentric factor ω , and the reduced temperature for each species, are combined through appropriate combinatorial relationships. The standard Peng-Robinson mixing rules are used.

$$a_M = \sum_{i=1}^N \sum_{j=1}^N y_i y_j a_{ij} \quad (\text{Eq 7})$$

$$b_M = \sum_{i=1}^N y_i b_i \quad (\text{Eq 8})$$

with: $a_{ij} = (1 - \delta_{ij})\sqrt{a_i a_j}$ and $a_{ii} = a_i$. The binary interaction parameter, δ_{ij} , is specific for the i-j binary pair. In these expressions, the a_i and b_i represent the pure component parameter values which are evaluated using:

$$a_i(\omega, T_r) = a(T_c)\alpha(\omega, T_r) \quad (\text{Eq 9})$$

$$a(T_c) = \frac{0.45724R^2 T_c^2}{P_c} \quad (\text{Eq 10})$$

$$\begin{aligned} \alpha(\omega, T_r) &= \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r}) \right]^2 \\ &= \left[1 + \kappa(1 - \sqrt{T_r}) \right]^2 \end{aligned} \quad (\text{Eq 11})$$

$$b_i = \frac{0.07780RT_c}{P_c} \quad (\text{Eq 12})$$

The Peng-Robinson equation is often written in terms of the compressibility, $Z = (PV/RT)$:

$$Z^3 + Z^2(B - 1) + Z(-3B^2 - 2B + A) + (B^3 + B^2 - AB) = 0 \quad (\text{Eq 13})$$

where A and B are defined as:

$$A = \frac{a_M P}{(RT)^2} \quad (\text{Eq 14})$$

$$B = \frac{b_M P}{RT} \quad (\text{Eq 15})$$

The use of this equation of state for evaluation of the fugacity coefficient of the solute in a supercritical fluid is well-documented in the literature (McHugh and Paulaitis 1980). Following the notation in Modell and Reid (1983), the fugacity coefficient for species i in solution is found through:

$$\begin{aligned} \ln(\hat{\phi}_i) &= \frac{b_i}{b_M} (Z - 1) - \ln(Z - B) \\ &+ \frac{A}{2\sqrt{2}B} \left(\frac{2 \sum_k y_k a_{ik}}{a_M} - \frac{b_i}{b_M} \right) \ln \left[\frac{Z + B(1 - \sqrt{2})}{Z + B(1 + \sqrt{2})} \right] \end{aligned} \quad (\text{Eq 16})$$

The prediction of solubility by this set of equations requires an iterative approach. In general, the temperature and pressure are known, as well as an estimate of the solubility, y_i . If experimental data are not available for use as the initial estimate, then an estimate is calculated by assuming that ideal behavior is valid (i.e., $y_i = P_i^{\text{sat}} / P$). The estimated y_i is then used with the given temperature to evaluate the pure component and mixture parameters. The compressibility is then determined through Equation 13 using the given T and P with the mixture parameters through solution of the cubic equation of state. In this implementation, the cubic equation is solved analytically. The compressibility is substituted into the expression for the fugacity coefficient, Equation 16, along with the necessary pure component and mixture parameters. The predicted solubility is then calculated through Equation 5. The iterative procedure is continued until the predicted solubility at the end of an iteration is equal to the estimate at the start of the iteration to within some prescribed tolerance.

4 Estimation of Critical Properties and Other Required Thermodynamic Information

Estimation of the critical properties and other required thermodynamic information was undertaken for the energetic compounds RDX, HMX, and CL20. Since a limited amount of pertinent data was available for RDX and HMX (i.e., critical temperature, critical volume, vapor pressure), the estimation of properties for these compounds could serve as a baseline to establish the validity of the estimation procedures used and thus provide for greater confidence in the estimates obtained for CL20. Although CL20 (Figure 1) is a much more complex molecule when compared with RDX (Figure 2) or HMX (Figure 3), all three molecules contain -NO_2 groups, individually attached to a ring >N- group.

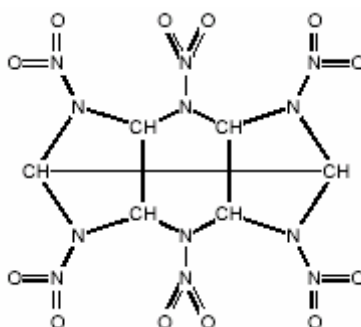


Figure 1. Molecular structure of CL20.

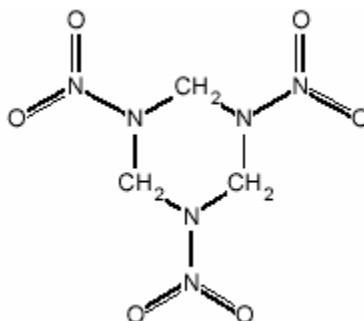


Figure 2. Molecular structure of RDX.

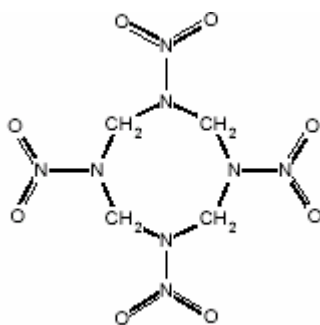


Figure 3. Molecular structure of HMX.

Group contribution methods were used to estimate the necessary values. Table 3 shows the group decomposition for these three compounds.

Table 3. Group decomposition of energetic molecules.

Group ID	CL20	RDX	HMX
	Number of Type	Number of Type	Number of Type
>N- (ring)	6	3	4
-NO ₂	6	3	4
CH (ring)	6		
CH ₂ (ring)		3	4

The method of Stein and Brown (1994) was used to estimate the normal boiling point for each compound. This method is an extension of Joback's method (Joback and Reid 1987) for estimation of the normal boiling point. Stein and Brown's extension specifically involves inclusion of additional groups and revision of Joback and Reid's groups into smaller subdivisions. Of interest in this work is the inclusion of the >N- (ring) group. For this group, the contributions to critical temperature and pressure were identical to those for a >N- (non-ring) group, but were different for the normal boiling point. Stein and Brown use the original relation of Joback and Reid, given as Equation 17:

$$T_b = 198.2 + \sum_i n_i g_i \quad (\text{Eq 17})$$

An additional refinement to the estimate is also given by Stein and Brown and was used in this work. For estimated normal boiling points for 700 K and below, the corrected boiling point is given by:

$$T_b(\text{corr}) = T_b - 94.84 + 0.5577T_b - 0.0007705T_b^2 \quad (\text{Eq 18})$$

Above 700 K, the corrected boiling point is given by:

$$T_b(\text{corr}) = T_b + 282.7 - 0.5209T_b \quad (\text{Eq 19})$$

Estimated normal boiling points calculated in this work for the compounds of interest are shown in Table 4.

Table 4. Estimated normal boiling points.

Compound	T_b Estimate (K)	$T_b(\text{corr})$ Estimate (K)
RDX	717.8	626.6
HMX	891.0	709.6
CL20	1208.7	861.8

The estimation of critical temperature was accomplished using Joback's method (Joback and Reid 1987) as implemented in the Cranium software (Molecular Knowledge Systems, Inc., Bedford, NH). This estimation technique requires the use of the normal boiling point; thus, the values shown in Table 4 were used. Table 5 shows estimates for the critical temperature for the compounds of interest.

The critical temperature estimated for RDX, 842.7 K, using the $T_b(\text{corr})$ estimate is in excellent agreement with the experimental value of 567 °C (840 K) reported by Maksimov (1992). Similarly, the critical temperature estimated for HMX, 913.5 K, using the $T_b(\text{corr})$ estimate is in good agreement with the experimental value of 654 °C (927 K) reported by Maksimov (1992).

Table 5. Estimated critical temperatures.

Compound	Critical Temperature, T_c Estimated using T_b (K)	Critical Temperature, T_c Estimated using $T_b(\text{corr})$ (K)
RDX	965.4	842.7
HMX	1147.1	913.5
CL20	1483.6	1057.8

The estimation of critical pressure was also accomplished using Joback's method (Joback and Reid 1987) as implemented in the Cranium program. No literature data for the critical pressure were identified for the compounds of interest. Table 6 shows estimates for the critical temperature for the compounds of interest.

Table 6. Estimated critical pressure.

Compound	Critical Pressure, P_c (bar)
RDX	58.0
HMX	53.0
CL20	48.9

In addition to the critical properties (temperature and pressure), the acentric factor, defined as vapor pressure of the compound at a reduced pressure of 0.7, is used in describing the temperature dependence of the attraction term in the Peng-Robinson equation of state. Thus, estimation of the acentric factor was also required for the compounds of interest. Poling et al. (2001) recommend the estimation of the acentric factor using the three parameter Pitzer expansion:

$$\ln(P_{vp} / P_c) = f^{(0)} + \omega f^{(1)} + \omega^2 f^{(2)} \quad (\text{Eq 20})$$

Neglecting the second order term, this can be rearranged, as shown in Equation 21 to provide an estimate of the acentric factor using the critical point and the normal boiling point.

$$\omega = - \frac{\ln(P_c / 1.01325) + f^{(0)}(T_{br})}{f^{(1)}(T_{br})} \quad (\text{Eq 21})$$

where T_{br} is the reduced normal boiling point and pressure is in bar. The functions, $f^{(0)}(T_{br})$, $f^{(1)}(T_{br})$, and $f^{(2)}(T_{br})$ are the temperature dependent correlations developed by Ambrose and Walton (1989) for the three parameter corresponding states method for prediction of vapor pressure. These expressions are shown in Equations 22 to 24 (Poling et al. 2000).

$$f^{(0)}(T_r) = \frac{-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5}{T_r} \quad (\text{Eq 22})$$

$$f^{(1)}(T_r) = \frac{-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5}{T_r} \quad (\text{Eq 23})$$

$$f^{(2)}(T_r) = \frac{-0.64771\tau + 2.41539\tau^{1.5} - 4.26979\tau^{2.5} + 3.25259\tau^5}{T_r} \quad (\text{Eq 24})$$

In these expressions, τ is defined as $(1-T_r)$. For larger molecules, the inclusion of the second order term can be important. Thus, inclusion of the second order term gives rise to a quadratic equation that must be solved. This quadratic equation is in the form:

$$\omega^2 f^{(2)} + \omega f^{(1)} + f^{(0)} - \ln(1.01325/P_c) = 0 \quad (\text{Eq 25})$$

The acentric factor was estimated using the values of $T_b(\text{corr})$ shown in Table 4, and values of T_c from Table 5. Estimated values for each of the compounds of interest are shown in Table 7. These values are compared to a two-point extrapolation of the vapor pressure curve to obtain an estimate of the acentric factor. Assuming a linear relationship between $\log_{10}(P_r)$ and $1/T_r$ gives rise to the expression shown in Equation 26.

$$\log_{10}(P_r) = -\frac{B}{T_c} \left[\frac{1-T_r}{T_r} \right] \quad (\text{Eq 26})$$

where B is given by:

$$B = \frac{\log_{10}(P_c) - \log_{10}(P_{\text{nbp}})}{\frac{1}{T_{\text{nbp}}} - \frac{1}{T_c}} \quad (\text{Eq 27})$$

Using the estimated normal boiling point and the critical temperature and pressure, the reduced vapor pressure at a reduced temperature of $T_r = 0.7$ was evaluated and then used in the definition of the acentric factor. Estimated values for the acentric factor obtained using this method are also provided in Table 7.

Table 7. Estimated acentric factor.

Compound	Acentric Factor (Estimated Using Cranium)	Acentric Factor (Estimated Using Eq. 22–25)	Acentric Factor (Estimated Using Eq. 26 and 27)
RDX	1.25	1.22	1.19
HMX	1.57	1.66	1.80
CL20	2.40	2.38	2.18

The estimation of vapor pressure was also undertaken for the model compounds. Vapor pressure data were located for RDX, but data for HMX and CL20 were not identified through the literature search. Dionne et al. (1986) report the vapor pressure of RDX as

$$\log_{10}(P_{vp}) = 22.50 - \frac{6473}{T} \quad (\text{Eq 28})$$

where P_{vp} is in parts per trillion (v/v) and T is in K. This correlation was based on their measurements over the temperature range of 37 to 102 °C combined with literature data from three other sources. A second expression for the vapor pressure of RDX was (U.S. Dept. of Labor 2003):

$$\log_{10}(P_{vp}) = 14.14 - \frac{6785}{T} \quad (\text{Eq 29})$$

where P_{vp} is in Pa and T is in K. These two expressions provide roughly the same estimates for the vapor pressure of RDX over the temperature range of interest.

Poling et al. (2001) recommend the use of the corresponding states method with the Ambrose-Walton expressions for the estimation of vapor pressure. The relevant expressions are:

$$\ln(P_{vp,r}) = f^{(0)} + \omega f^{(1)} + \omega f^{(2)} \quad (\text{Eq 30})$$

where $P_{vp,r}$ is the reduced vapor pressure, $f^{(0)}$ is given by Equation 22, $f^{(1)}$ by Equation 23, and $f^{(2)}$ by Equation 24. Vapor pressures were estimated according to Equation 30 using the values for the acentric factor given in Table 7. Vapor pressures for RDX estimated using this technique differed from the available literature data by a factor of 10^3 . Vapor pressures were also estimated according to Equation 26. The estimated vapor pressure is compared to the available literature data for RDX in Figure 4. The estimates are in good agreement with the literature data over the range of 25 °C to approximately

60 °C. Above 60 °C, the estimated vapor pressure and the literature data diverge, with the estimated vapor pressure being almost half that reported in the literature at 80 °C. For prediction of solubility in supercritical CO₂, it is anticipated that the temperature range of interest is between approximately 35 and 60 °C. Thus, Equation 26 was used to estimate the vapor pressure of CL20. These estimated vapor pressures were then used in the evaluation of the solubility of CL20 in supercritical CO₂ and are plotted in Figure 5.

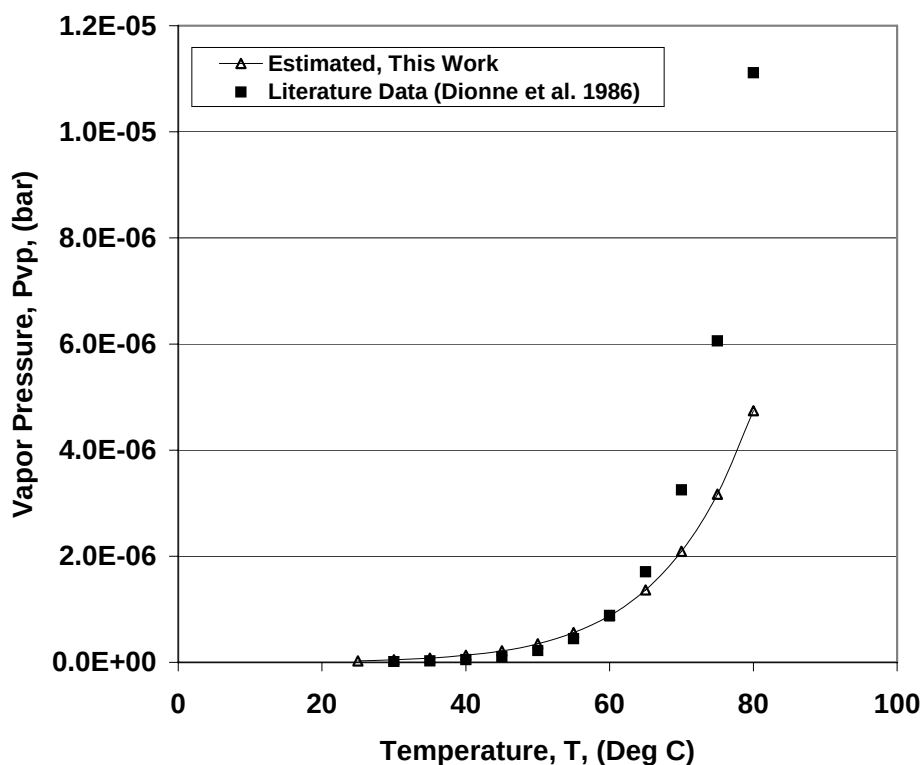


Figure 4. Comparison of estimated RDX vapor pressure with literature data.

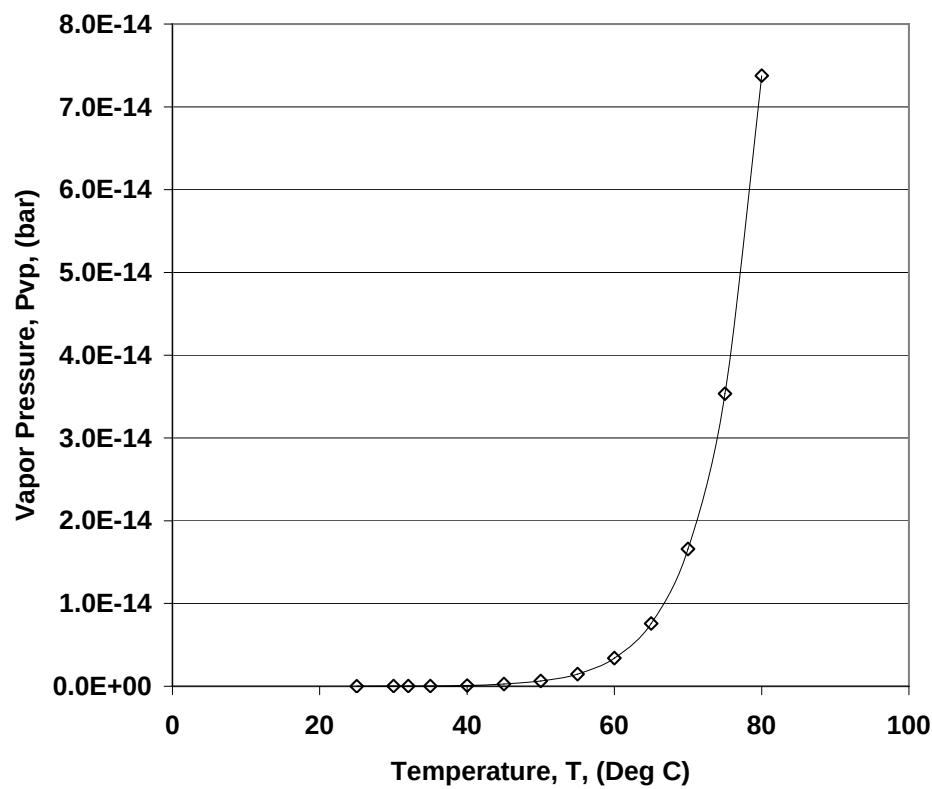


Figure 5. Estimated vapor pressure for CL20.

5 Validation of the Developed Code

The Fortran code was validated using the solubility of naphthalene and of biphenyl in supercritical CO₂. Data for these systems were measured by McHugh and Paulaitis (1980). For naphthalene in supercritical CO₂, the value of the interaction parameter, δ_{12} , was set to 0.103, while for biphenyl in supercritical CO₂, a value of 0.12 was used. These values for the interaction parameter were obtained by Schmitt (1984) by regression of the data of Tsehanskaya et al. (1964) for naphthalene, and the data of McHugh and Paulaitis for biphenyl. Figure 6 provides a comparison of the literature data to the predicted values for naphthalene, while Figure 7 provides the comparison of literature data to predicted values for biphenyl. The predicted values are in fair agreement with the literature data for naphthalene in the range of pressures from approximately the critical pressure of CO₂ (~ 74 bar) to approximately 200 bar. The predicted solubilities at 55 °C, corresponding to the highest pressures examined by McHugh and Paulaitis, diverge from the experimental data. A reason for the discrepancy is that Schmitt (1984) reported different values of the interaction parameter for each set of isothermal data. Thus, the same interaction parameter did not provide the best representation of data for differing isotherms.

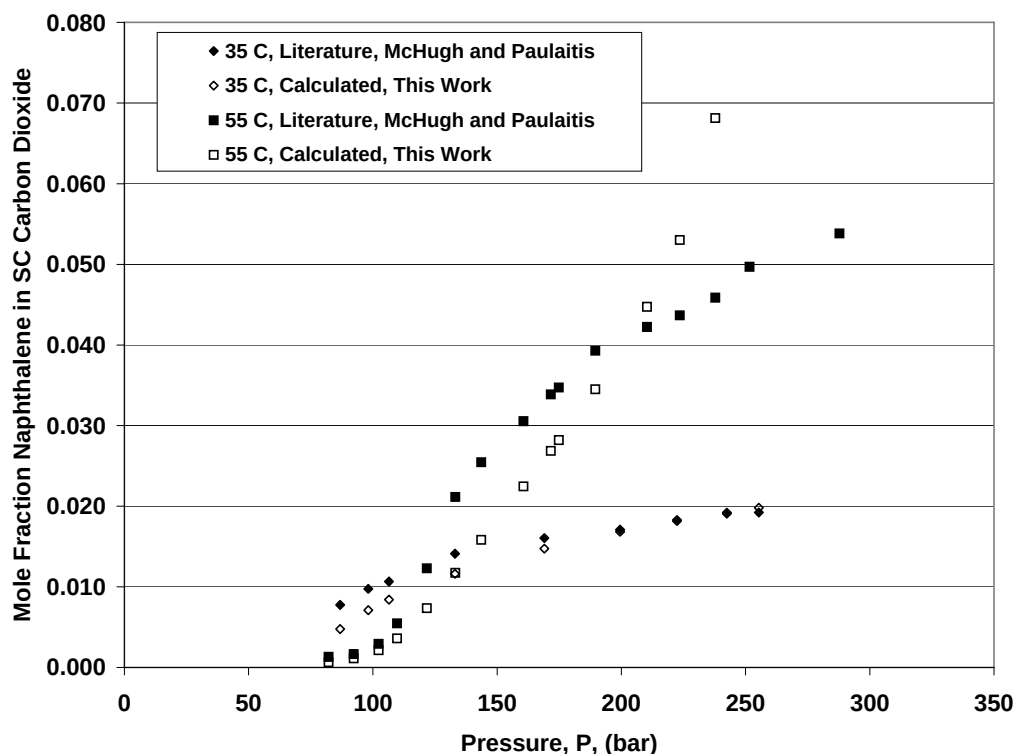


Figure 6. Solubility of naphthalene in supercritical CO₂; comparison of literature data and calculated values.

For biphenyl in supercritical CO₂, the agreement between predicted and measured values is much better, which is most likely due to the use of an interaction parameter for the data set that had been obtained through regression of the same data set. The primary motivation of using these well-known data sets to provide validation and verification of the developed code was that the performance of the code could be more easily established since all required information (i.e., critical temperature, critical pressure, acentric factor, vapor pressure, saturated molar volume) was available for the solutes (naphthalene and biphenyl) as well as the solvent (CO₂).

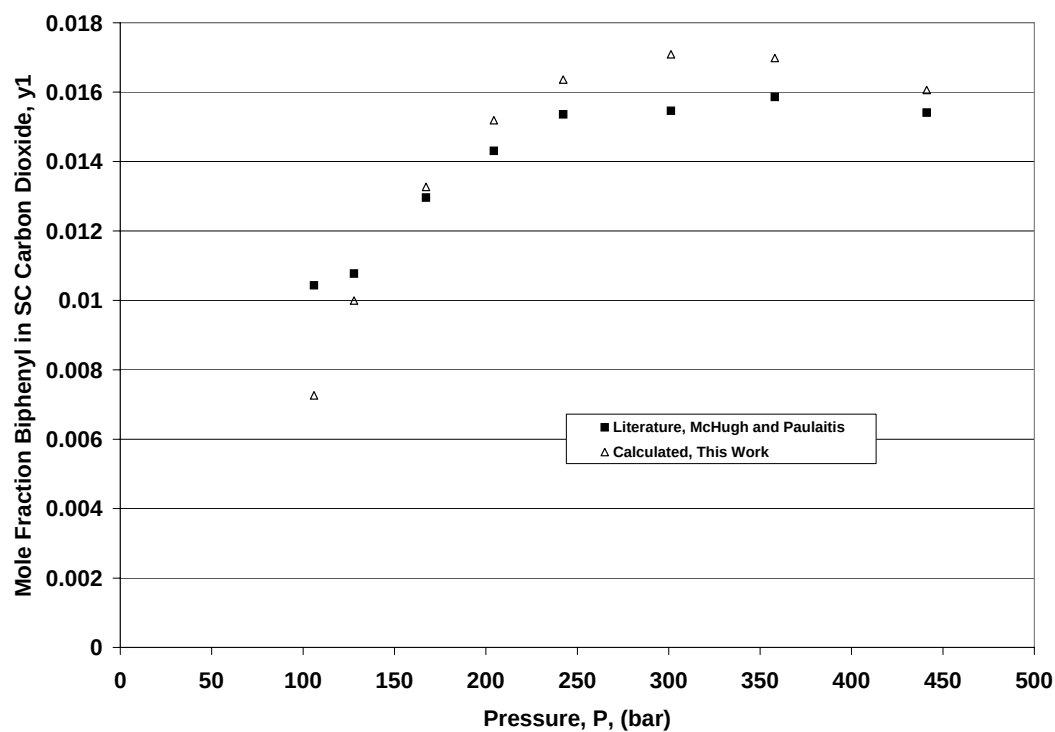


Figure 7. Solubility of biphenyl in supercritical CO₂ comparison of literature data and calculated values at 35.8 °C.

6 Solubility of Explosives in Supercritical CO₂

Comparison of SCF Predictions for RDX in CO₂ With Available Literature Data

The solubility of RDX in subcritical and supercritical carbon dioxide was reported by Morris (1998). The reported values (in mg RDX/g CO₂) were converted to mole fractions for comparison with code predictions. The critical temperature, critical pressure, and acentric factor estimated for this work were used along with the vapor pressure reported by Dionne et al. (1986) to predict the solubility of RDX. The initial estimate used in the iterative code for the solubility was the experimental value reported by Morris at the conditions of interest. There is little agreement between the literature data and the predictions, as shown in Figure 8. The literature solubilities are quite small, with magnitudes between 10^{-7} and 10^{-5} , while the predicted solubilities were larger with magnitudes between 10^{-7} and 10^{-3} . This is most likely due to the vapor pressure expression employed. Error in the vapor pressure translates directly into error in the predicted solubility, as evidenced through Equation 5. If the vapor pressure is overestimated by a factor of 2, then the predicted solubility will be overestimated to the same degree. Accurate measurement of the vapor pressure of the explosive compound is an essential requirement for reliable predictions of the solubility of an explosive in supercritical CO₂.

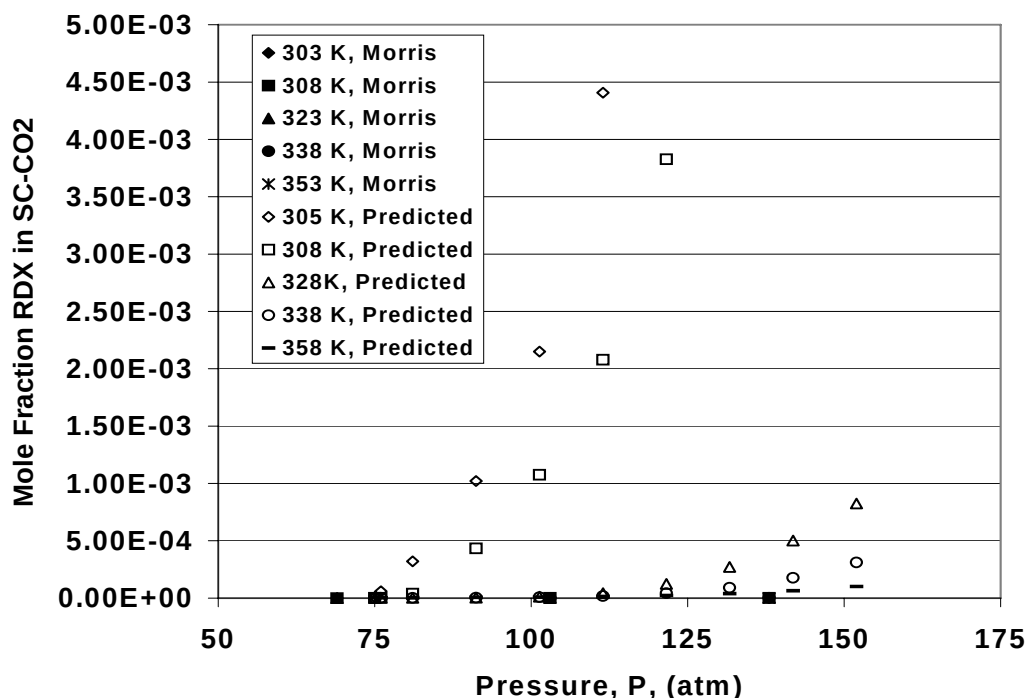


Figure 8. Solubility of RDX in subcritical and supercritical CO₂; comparison of predictions with literature data.

SCF Predictions for CL20 in Supercritical CO₂

The solubility of CL20 in supercritical CO₂ was predicted using the developed Fortran code. The estimated critical temperature, critical pressure, and acentric factor were used in the code along with Equation 26 for estimation of the vapor pressure. A two-point fit (critical point, normal boiling point) allowed estimation of the coefficient B in Equation 26. Since no experimental measurements were available, the initial estimate of the solubility was set to 1.0e-16. Solubility was predicted over the temperature range of 305.15 to 368.15 K and over the pressure range of 74 to 150 atmospheres (atm). The temperature range corresponds to a range of reduced temperature of 1.003 to 1.21 with respect to CO₂, while the pressure range corresponds to a reduced pressure range of 1.01 to 2.06. The estimated solubilities are shown in Figure 9 (low temperature) and Figure 10 (high temperature). In general, as the temperature increases, the solubility decreases, while, as the pressure increases, the solubility increases. The predicted behavior is markedly different near the critical point of CO₂ when compared with the behavior of naphthalene in supercritical CO₂. An examination of Figure 6 indicates that, as the pressure is increased from near the critical point to higher pressures, the solubility of naphthalene shows an inflection point, followed by a

significant increase in the solubility over a fairly narrow pressure range. This increase is influenced to a significant degree by the vapor pressure of the solute. For CL20, the estimated vapor pressures are extremely small, on the order of 10^{-18} at ambient temperature, increasing to 10^{-13} at 368.15 K. Thus, the predicted solubilities are also small (range of 10^{-13} to 10^{-6}), with the highest solubility predicted for 308.15 K (35°C) and 150 atm. In the region of temperature nearest the critical point of CO₂, the influence of the supercritical fluid is stronger. It would be most desirable to operate in this region of 35–50 °C if one is interested in maximizing the solubility of the solute, CL20, in the CO₂.

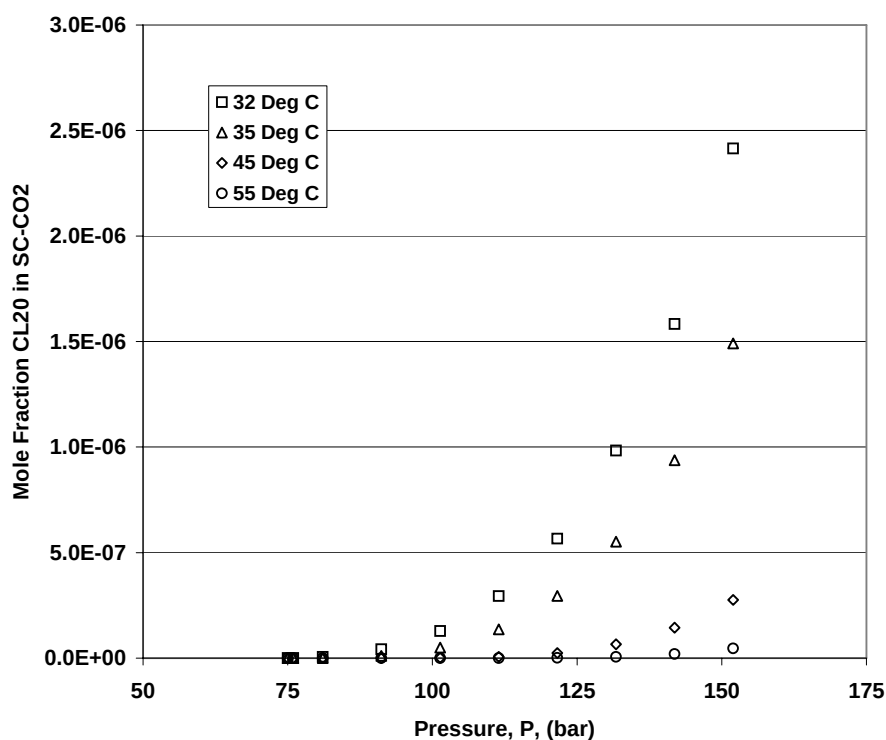


Figure 9. Predicted solubility of CL20 in supercritical CO₂ – low temperature range.

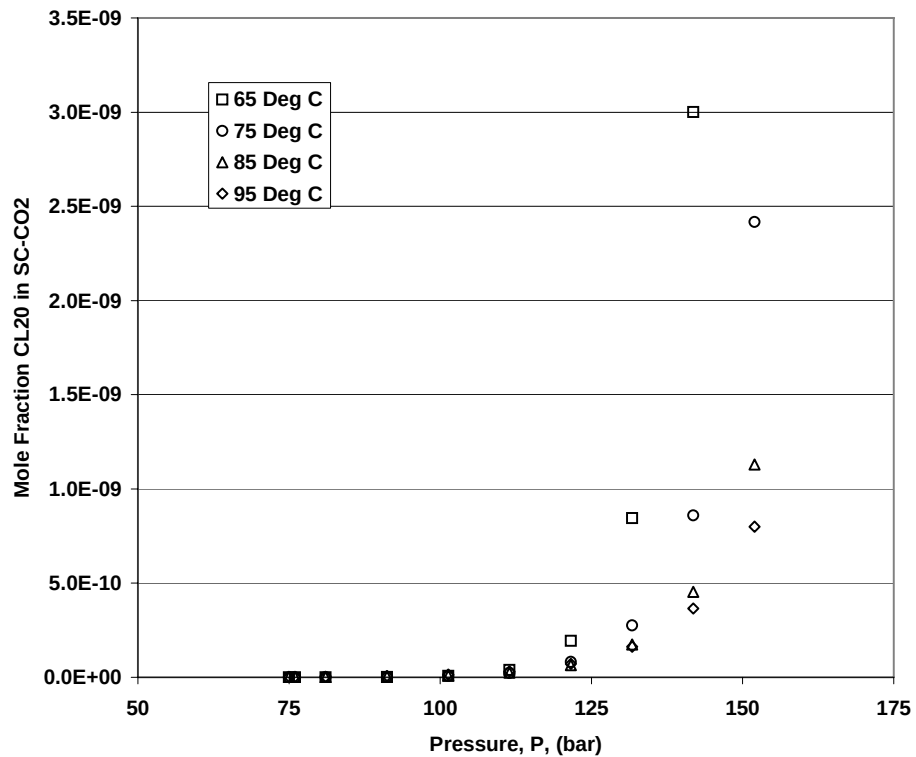


Figure 10. Predicted solubility of CL20 in supercritical CO₂ – high temperature range.

7 Conclusion

A comprehensive search of the literature revealed limited data that could be used to validate the approach taken in this work for estimation of necessary thermodynamic properties. The estimation of normal boiling point, critical temperature, critical pressure, acentric factor, and vapor pressure for CL2O was accomplished using available group contribution techniques and property definitions. While CL2O is a very complex species, comparison of estimated critical temperature for RDX and HMX to values reported in the literature provides a measure of confidence in the estimated values for CL2O. All three species are composed of similar molecular groups, the primary difference being the presence of -CH (ring) groups in CL2O and -CH₂ (ring) groups in RDX and HMX.

A Fortran code was developed for the estimation of the solubility of a solute in supercritical CO₂. Performance of the code was validated using the data of McHugh and Paulaitis (1980) for naphthalene and biphenyl solubilities in supercritical CO₂. The prediction of solubility for the explosive RDX in supercritical CO₂ was performed and the predicted values compared with available literature data. The lack of agreement between the predicted and literature data is most likely due to the uncertainty associated with the vapor pressure of RDX.

Solubilities for CL2O in supercritical CO₂, over a reduced temperature range of 1.003 to 1.21 and a reduced pressure range of 1.01 to 2.06, were predicted using the developed code. These predictions lead to two primary conclusions. First, the solubility estimates are very strongly influenced by the vapor pressure. Experimental measurement of the vapor pressure of CL2O should be performed. Second, the conditions that appear to be most viable for maximizing the solubility of CL2O in supercritical CO₂ are the lowest supercritical temperature examined (35 °C) and the highest pressure (150 atm).

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Appendix A: Validation of FORTRAN Code

Table A1. Calculated solubility of naphthalene in supercritical CO₂.

Pressure (atm)	Solubility T = 308.15 K	Pressure (atm)	Solubility T = 328.15 K
85.7	0.0047556	81.1	0.000666
96.9	0.0071149	91.1	0.001136
105.1	0.0084182	101	0.002154
131.3	0.0116050	108.3	0.003600
166.8	0.0147523	120.1	0.007367
196.9	0.0168408	131.5	0.011752
219.5	0.0181707	141.8	0.015812
239.3	0.0192039	158.5	0.022442
252	0.0198117	169.4	0.026870
		172.6	0.028199
		187.1	0.034487
		207.6	0.044719
		220.6	0.053024
		234.7	0.068143

Table A2. Calculated solubility of biphenyl in supercritical CO₂.

Pressure (atm)	Solubility T = 308.95 K
104.6	0.007263
126.2	0.009996
165.1	0.013270
201.7	0.015190
239.1	0.016361
297.3	0.017091
353.4	0.016984
435.4	0.016064

Appendix B: Calculated Solubilities for Explosive Compounds in Supercritical CO₂

Table B1. Calculated solubility of RDX in supercritical CO₂.

Pressure (atm)	Pressure (bar)	305.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K	358.15 K	368.15 K
74	74.9805	7.84e-06	1.80e-06	9.19e-07	9.89e-07	1.30e-06	1.88e-05	2.82e-06	4.32e-06
75	75.9938	6.03e-05	2.42e-06	1.03e-06	1.07e-06	1.38e-06	1.97e-06	2.93e-06	4.47e-06
80	81.0600	3.21e-04	3.91e-05	1.98e-06	1.63e-06	1.89e-06	2.52e-06	3.59e-06	5.28e-06
90	91.1925	1.02e-03	4.35e-04	1.13e-05	4.27e-06	3.76e-06	4.29e-06	5.52e-06	7.54e-06
100	101.3250	2.15e-03	1.08e-03	8.18e-05	1.33e-05	8.08e-06	7.64e-06	8.74e-06	1.10e-05
110	111.4575	4.41e-03	2.08e-03	2.82e-04	4.41e-05	1.84e-05	1.41e-05	1.42e-05	1.64e-05
120	121.5900		3.83e-03	6.18e-04	1.24e-04	4.22e-05	2.65e-05	2.33e-05	2.46e-05
130	131.7225			1.11e-03	2.73e-04	9.09e-05	4.94e-05	3.85e-05	3.71e-05
140	141.8550			1.80e-03	5.03e-04	1.77e-04	8.91e-05	6.29e-05	5.57e-05
150	151.9875			2.78e-03	8.25e-04	3.10e-04	1.52e-04	1.00e-04	8.30e-05

Table B2. Calculated solubility of CL20 in supercritical CO₂.

Pressure (atm)	Pressure (bar)	305.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K	358.15 K	368.15 K
74	74.9805	6.27e-12	4.07e-13	1.16e-13	1.33e-13	2.22e-13	4.36e-13	9.24e-13	2.03e-12
75	75.9938	2.43e-10	7.15e-13	1.46e-13	1.56e-13	2.51e-13	4.81e-13	1.00e-12	2.18e-12
80	81.0600	5.55e-09	1.27e-10	5.09e-13	3.53e-13	4.67e-13	7.94e-13	1.53e-12	3.12e-12
90	91.1925	4.11e-08	1.04e-08	1.41e-11	2.29e-12	1.80e-12	2.31e-12	3.68e-12	6.56e-12
100	101.3250	1.28e-07	4.92e-08	5.83e-10	2.03e-11	8.00e-12	7.23e-12	9.28e-12	1.43e-11
110	111.4575	2.93e-07	1.36e-07	5.76e-09	1.99e-10	3.93e-11	2.40e-11	2.43e-11	3.17e-11
120	121.5900	5.66e-07	2.94e-07	2.38e-08	1.40e-09	1.94e-10	8.21e-11	6.50e-11	7.17e-11
130	131.7225	9.83e-07	5.51e-07	6.54e-08	6.17e-09	8.45e-10	2.75e-10	1.74e-10	1.63e-10
140	141.8550	1.58e-06	9.38e-07	1.44e-07	1.91e-08	3.00e-09	8.59e-10	4.54e-10	3.65e-10
150	151.9875	2.41e-06	1.49e-06	2.76e-07	4.65e-08	8.66e-09	2.42e-09	1.13e-09	8.00e-10

Appendix C: Developed FORTRAN Code for Estimation of Solubility of CL20 in Supercritical CO₂

Instructions for Use of Executable File

Input data are provided in the SCFIN.TXT file, which should exist in the same directory as the executable code. The format for the input data file is:

Card 1: Columns 1-3, I3 field, Number of data points (NDAT) to be evaluated (maximum value for NDAT is 100)

Card 2: NDAT+1: Columns 1-10, Temperature in Kelvin (F10.5 field)
Columns 11-20, Pressure in Atmospheres (F10.5 field)

Sample Input File

```
10
368.15    74.0
368.15    75.0
368.15    80.0
368.15    90.0
368.15   100.0
368.15   110.0
368.15   120.0
368.15   130.0
368.15   140.0
368.15   150.0
```

Output from the program is in tabular form. Temperature is in K, pressure is in bar, estimated solubility of CL20 is given as mole fraction CL20 in the CL20-CO₂ mixture.

Code for Executable File

```
C

C      PROGRAM TO EVALUATE THE SOLUBILITY OF A SOLUTE IN A SUPERCRITICAL
C      FLUID.
C
C      IMPLICIT REAL*8(A-H,O-Z)
C
C      COMMON /PARAM/ A1C,B1C,A2C,B2C
C
C      COMMON /PARAM1/ TC1,PC1,OMEGA1,TC2,PC2,OMEGA2,DEL12
C
C      COMMON /PARAM2/ A1,A2,A12,AMIX,B1,B2,BMIX,CAPAMIX,CAPBMIX
C
C      COMMON /PARAM3/ CAPA1,CAPA2,CAPB1,CAPB2
C
C      REAL*8 TEXP(100),PEXP(100),Y2FIN(100)
C
C      CHARACTER*10 INFILE,OUTFIL
C
C      INFILE="SCFIN.TXT"
C
C      OUTFIL="SCFOUT.TXT"
C
C      OPEN(UNIT=5,FILE=INFILE,ACTION="READ")
C
C      OPEN(UNIT=6,FILE=OUTFIL,ACTION="WRITE")
C
C      EXPERIMENTAL DATA ARE READ FROM FILE SCFIN.TXT
C
C      READ(5,8000) NDAT
C
C      8000 FORMAT(I3)
C
C      WRITE(6,9010)
C
C      9010 FORMAT(' ',2X,'INPUT DATA')
C
C      DO 10 J=1,NDAT
```

```
      READ(5,8001) TEXP(J),PEXP(J)

8001  FORMAT(2F10.5)

      PEXP(J)=PEXP(J)*1.01325D0

      WRITE(6,8002) J,TEXP(J),PEXP(J)

8002  FORMAT(' ',2X,I3,2X,'T =',D15.6,'K',2X,'P =',D15.6,'BAR')

10  CONTINUE

C

C   PROPERTIES OF THE SUPERCRITICAL FLUID ARE NEEDED TO EVALUATE EOS

C   PARAMETERS - COMPONENT 1 IS THE SOLVENT; COMPONENT 2 IS THE SOLUTE

C

      TC1=304.12D0

      PC1=73.74D0

      OMEGA1=0.225D0

      TC2=1058.0d0

      PC2=48.9d0

      OMEGA2=2.18d0

      DEL12=0.0D0

C

C   UNIVERSAL GAS CONSTANT DEFINED

C

      RG=83.14D0

C

C   EOS PARAMETERS MUST BE EVALUATED

C
```

```
A1C=0.45724D0*RG*RG*TC1*TC1/PC1

B1C=0.07780D0*RG*TC1/PC1

A2C=0.45724D0*RG*RG*TC2*TC2/PC2

B2C=0.07780D0*RG*TC2/PC2

C

C      WRITE(6,200) A1C,B1C

C 200  FORMAT(' ',2X,'A1C =',F15.6,2X,'B1C =',F15.6)

C

C      WRITE(6,201) A2C,B2C

C 201  FORMAT(' ',2X,'A2C =',F15.6,2X,'B2C =',F15.6)

C

C      MAIN LOOP IN THE PROGRAM - THIS LOOP IS COMPLETED FOR EACH OF THE

C      NDAT POINTS.

C

      DO 1000 J=1,NDAT

      Y2=1.D-16

      Y1=1.D0-Y2

      T=TEXP(J)

      P=PEXP(J)

C

C      SUBROUTINE EOSROOT EVALUATES THE COMPRESSIBILITY OF THE FLUID

C      USING THE PENG-ROBINSON EQUATION OF STATE, GIVEN A VALUE FOR

C      TEMPERATURE AND PRESSURE

C
```

```
        ITER=1

C      WRITE(6,8007) J
C8007 FORMAT(' ', 'J =', I3)

      20 CALL EOSROOT(T,P,Y1,Y2,Z,DISC)

        IF(DISC.LE.(0.D0)) THEN

          GO TO 1000

        ENDIF

C      WRITE(6,8005)
C8005 FORMAT(' ', 2X, 'FINISHED EOSROOT')

        CALL FUGEVAL(T,P,Y1,Y2,Z,PHI2H)

C      WRITE(6,8006)
C8006 FORMAT(' ', 2X, 'FINISHED FUGEVAL')

        CALL SOLUEST(T,P,Y1,Y2,Z,PHI2H,Y2EST)

        DIFF=DABS((Y2-Y2EST)/Y2EST)

        IF(DIFF.LE.(1.D-16)) THEN

C          WRITE(6,8003) T,P,Y1,Y2
C8003 FORMAT(' ', 2X, 'T =', D15.6, 2X, 'P =', D15.6, 2X, 'Y1 =', D15.6, 2X, 'Y2= '
C      $, D15.6)
C          WRITE(6,8004) Z, PHI2H, Y2EST
C8004 FORMAT(' ', 2X, 'Z =', D15.6, 2X, 'PHI2H =', D15.6, 2X, 'Y2EST =', D15.6)

          Y2FIN(J)=Y2EST

          GO TO 1000

        ELSE

          ITER=ITER+1
```



```
C      WRITE(6,8003) T,P,Y1,Y2

C      WRITE(6,8004) Z,PHI2H,Y2EST

      Y2=Y2EST

      Y1=1-Y2

      GO TO 20

      ENDIF

1000 CONTINUE

C

C      OUTPUT OF FINAL RESULTS

C

      WRITE(6,2003)

2003 FORMAT(' ')

      WRITE(6,2003)

      WRITE(6,2003)

      WRITE(6,2001)

2001 FORMAT(' ',3X,' J ',4X,'Temperature (K)',2X,'Pressure (bar)',2X,
           '$Solubility (mol CL20/mol mixture)')

      WRITE(6,2003)

      DO 2000 J=1,NDAT

      WRITE(6,2002) J, TEXP(J),PEXP(J),Y2FIN(J)

2002 FORMAT(' ',4X,I2,4X,F15.2,2X,F15.2,2X,D21.6)

2000 CONTINUE

      STOP

      END
```

CAPA2, CAPB1, CAPB2

C

C IN THE SUPERCRITICAL REGION, ONLY A SINGLE ROOT SHOULD BE PRESENT
C FOR THE CUBIC EQUATION OF STATE. THE ROOT IS DETERMINED USING THE
C THE STANDARD ANALYTIC FORM OF A THIRD ORDER POLYNOMIAL

C

C PARAMETER A1 = A1C*ALPHA(OMEGA1, TR1) IS EVALUATED

C

RG=83.14D0

TR1=T/TC1

EKAPPA1=0.37464D0+1.54226D0*OMEGA1-0.26992D0*OMEGA1*OMEGA1

TERM1=1.D0-DSQRT(TR1)

ALPHA1=(1.D0+EKAPPA1*TERM1)**2

A1=A1C*ALPHA1

B1=B1C

C

C PARAMETER A2 = A2C*ALPHA(OMEGA2, TR2) IS EVALUATED)

C

TR2=T/TC2

EKAPPA2=0.37464D0+1.54226D0*OMEGA2-0.26992D0*OMEGA2*OMEGA2

TERM2=1.D0-DSQRT(TR2)

ALPHA2=(1.D0+EKAPPA2*TERM2)**2

A2=A2C*ALPHA2

B2=B2C

C

C WRITE(6,300) ALPHA1,ALPHA2

C 300 FORMAT(' ', 'ALPHA1 =', F15.6, 2X, 'ALPHA2 =', F15.6)

C WRITE(6,301) A1,B1

C 301 FORMAT(' ', 2X, D15.6, 2X, D15.6)

C WRITE(6,301) A2,B2

C

$CAPA1 = A1 * P / ((RG * T)^{**2})$

$CAPB1 = (B1 * P) / (RG * T)$

$CAPA2 = A2 * P / ((RG * T)^{**2})$

$CAPB2 = (B2 * P) / (RG * T)$

C WRITE(6,302) CAPA1,CAPB1

C 302 FORMAT(' ', 2X, D15.6, 2X, D15.6)

C WRITE(6,302) CAPA2,CAPB2

C

C MIXTURE PARAMETERS ARE EVALUATED USING MIXING RULES

C

$A12 = (1.D0 - DEL12) * (DSQRT(A1 * A2))$

$AMIX = Y1 * Y1 * A1 + 2 * Y1 * Y2 * A12 + Y2 * Y2 * A2$

$BMIX = Y1 * B1 + Y2 * B2$

$CAPAMIX = AMIX * P / ((RG * T)^{**2})$

$CAPBMIX = (BMIX * P) / (RG * T)$

C WRITE(6,303) A12

C 303 FORMAT(' ', 2X, 'A12 =', D15.6)

```
C      WRITE(6,304) AMIX,BMIX

C 304  FORMAT(' ',2X,'AMIX =',D15.6,2X,'BMIX =',D15.6)

C      WRITE(6,305) CAPAMIX,CAPBMIX

C 305  FORMAT(' ',2X,'CAPAMIX =',D15.6,2X,'CAPBMIX =',D15.6)

C

C      CUBIC FORM OF PENG-ROBINSON EQUATION OF STATE IS SOLVED FOR THE

C      COMPRESSIBILITY USING ANALYTIC SOLUTION OF THE CUBIC EQUATION

C

10  COEF1=CAPBMIX-1.D0

      COEF2=-3.D0*CAPBMIX*CAPBMIX-2.D0*CAPBMIX+CAPAMIX

      COEF3=CAPBMIX*CAPBMIX*CAPBMIX+CAPBMIX*CAPBMIX-CAPAMIX*CAPBMIX

      QP=(3.D0*COEF2-COEF1*COEF1)/9.D0

      RP=(9.D0*COEF1*COEF2-27.D0*COEF3-2*COEF1*COEF1*COEF1)/54.D0

      DISC=(QP**3)+(RP**2)

C      WRITE(6,309) COEF1,COEF2,COEF3,QP,RP,DISC

C 309  FORMAT(' ',6(2X,F10.5))

C      IF(DISC.LE.0) THEN

C          WRITE(6,308)

C 308  FORMAT(' ',2X,'DISCRIMINANT IS LESS THAN OR EQUAL TO ZERO')

C          GO TO 12

C      ENDIF

      DISCRT=DSQRT(DISC)

      ARG1=RP+DISCRT

      ARG2=RP-DISCRT
```

```

      IF(ARG1.LT.(0.D0)) THEN

        ARG1=DABS(ARG1)

        SP=-1.D0*(ARG1**(1.D0/3.D0))

      ELSE

        SP=(ARG1)**(1.D0/3.D0)

      ENDIF

      IF(ARG2.LT.(0.D0)) THEN

        ARG2=DABS(ARG2)

        TP=-1.D0*(ARG2**(1.D0/3.D0))

      ELSE

        TP=(ARG2)**(1.D0/3.D0)

      ENDIF

      Z=SP+TP-(COEF1/3.D0)

C      WRITE(6,310) DISCRT,SP,TP,Z

C 310 FORMAT(' ',4(2X,D15.7))

12 RETURN

      END

C

C*****

C

      SUBROUTINE FUGEVAL(T,P,Y1,Y2,Z,PHI2H)

      IMPLICIT REAL*8(A-H,O-Z)

      COMMON /PARAM/ A1C,B1C,A2C,B2C

      COMMON /PARAM1/ TC1,PC1,OMEGA1,TC2,PC2,OMEGA2,DEL12

```

```

COMMON /PARAM2/ A1, A2, A12, AMIX, B1, B2, BMIX, CAPAMIX, CAPBMIX

COMMON /PARAM3/ CAPA1, CAPA2, CAPB1, CAPB2

C

C THIS SUBROUTINE EVALUATES THE FUGACITY FOR THE SOLUTE IN SOLUTION

C

TERM1=Z+CAPBMIX*(1.D0-DSQRT(2.D0))

TERM2=Z+CAPBMIX*(1.D0+DSQRT(2.D0))

TERM3=(2*(Y1*A12+Y2*A2)/AMIX)-(B2/BMIX)

TERM4=CAPAMIX/(2.D0*DSQRT(2.D0)*CAPBMIX)

TERM5=TERM4*DLOG(TERM1/TERM2)

TERM6=(B2/BMIX)*(Z-1.D0)

TERM7=-DLOG(Z-CAPBMIX)

DLNPHI=TERM6+TERM7+TERM3*TERM5

PHI2H=DEXP(DLNPHI)

C WRITE(6,100) TERM1, TERM2, TERM3,

C WRITE(6,100) TERM4, TERM5, TERM6

C WRITE(6,100) TERM7, DLNPHI, PHI2H

C 100 FORMAT(' ', 5(2X, D15.6))

RETURN

END

C

C

C

SUBROUTINE SOLUEST(T, P, Y1, Y2, Z, PHI2H, Y2EST)

```

```
      IMPLICIT REAL*8(A-H,O-Z)

      COMMON /PARAM/ A1C,B1C,A2C,B2C

      COMMON /PARAM1/ TC1,PC1,OMEGA1,TC2,PC2,OMEGA2,DEL12

      COMMON /PARAM2/ A1,A2,A12,AMIX,B1,B2,BMIX,CAPAMIX,CAPBMIX

      COMMON /PARAM3/ CAPA1,CAPA2,CAPB1,CAPB2

C

C      THIS SUBROUTINE ESTIMATES THE SOLUBILITY OF THE SOLUTE IN THE
C      SUPERCRITICAL PHASE.  VALUES FOR THE VAPOR PRESSURE OF THE SOLUTE
C      AS A FUNCTION OF TEMPERATURE MUST BE AVAILABLE.  ALSO NEEDED IS
C      THE SATURATED LIQUID VOLUME AT THE TEMPERATURE OF INTEREST.  BOTH
C      VAPOR PRESSURE AND SATURATED LIQUID VOLUME ARE USED TO EVALUATE
C      THE POYNTING FACTOR.
C
C      EVALUATION OF VAPOR PRESSURE
C

      RG=83.14D0
      BVP=7857.52D0

      VPLOG10=(-BVP/TC2)*(1-(T/TC2))/(T/TC2)

      VP=10.D0**(VPLOG10)

      P2SAT=VP*PC2

C      WRITE(6,200) P2SAT
C 200 FORMAT(' ',2X,'P2SAT =',D15.6)

      V2SAT=438.18d0/2.0d0

C      WRITE(6,201) V2SAT
C 201 FORMAT(' ',2X,'V2SAT =',D15.6)
```

$$Y2EST = (P2SAT/P) * (1.D0/PHI2H) * DEXP(V2SAT * (P - P2SAT) / (RG * T))$$

C WRITE(6,202) Y2EST

C 202 FORMAT(' ',2X,'Y2EST =',D15.6)

 RETURN

 END

