

SOLUBILITY AND PHASE BEHAVIOR OF CL20 AND RDX IN SUPERCRITICAL CARBON DIOXIDE

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ABSTRACT

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) [Nielson, et al. 1998]. The combustion and detonation characteristics of CL20 can be improved if it is formed into nanoparticles of uniform size. A new, promising process for particulation of materials utilizes environmentally benign compressed gases as either solvents or anti-solvents. Predictive models are required to describe the solubility and phase behavior of supercritical solutions of CL20 and supercritical carbon dioxide and for process simulation and development. Here, the solubility of CL20 in supercritical carbon dioxide was evaluated using the Peng-Robinson cubic equation of state. Critical properties, vapor pressure, and other required thermodynamic properties were estimated using a variety of available estimation techniques, including the group contribution methods of Lydersen and of Joback. A Fortran program to predict the solubility of CL20 was developed during the course of this project. The program was validated using available literature data for the solubility of naphthalene and of biphenyl in supercritical carbon dioxide. 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 carbon dioxide reported in the literature were also used to establish the validity of the estimation approach. Solubility was predicted over the temperature range of 305.15 to 368.15 K and over the pressure range of 74 to 150 atm. In general, as the temperature increases, the solubility decreases, while as the pressure increases, the solubility increases. 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 carbon dioxide, the influence of the supercritical fluid is stronger. It would be most desirable to operate in this region if one is interested in maximizing the solubility of the solute, CL20, in the carbon dioxide.

1. INTRODUCTION

The Army is interested in developing a green process to produce nanocrystalline ($\leq 300\text{nm}$) particles of the high energy explosive compound ϵ -CL20 (2,4,6,8,10,12-Hexanitro-2,4,5,8,10,12-hexaazaisowurtzitane). The combustion and detonation characteristics of the CL20 can be improved if it is formed into nanoparticles of uniform size. Processes such as Supercritical Antisolvent process (SAS) and condensation with Rapid Expansion of Supercritical Solutions (RESS), Gas Antisolvent (GAS), and Supercritical Antisolvent with Enhanced mass transfer (SAS-EMTM) are potential green processes for producing ultrafine particles. In these processes, the material to be particulated will be dissolved (solubilized) into an environmentally benign solvent such as supercritical carbon dioxide and then condensed to ultrafine particles by reducing the pressure and temperature of the mixture.

Theoretical and/or predictive models are required for process simulation and to describe the solubility and phase behavior of the supercritical solutions of CL20 and supercritical carbon dioxide. Experimental data on the solubility and phase behavior of CL20 in supercritical carbon dioxide are not available. This paper presents a method to estimate the required vapor pressure data, other

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parameters required for the model, and predicted solubility of CL20 and its close cousin RDX.

2. LITERATURE REVIEW

A comprehensive literature review was conducted to identify sources of thermodynamic information for CL20 and similar energetic compounds, including RDX and HMX. These energetic compounds were included since they have been used as explosive agents for a longer time and, thus, there would most likely be more information available. The available data for these compounds could then be used to validate estimation techniques for the thermodynamic properties of CL20. Available information on the three compounds was compiled using the 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. Two computerized database searches were conducted, yielding the following relevant information.

2.1 Beilstein Database

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, melting point and enthalpy of formation. 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	.000036 - .0004 mm Hg @ 110.6°C -138.5°C	Edwards (1953)
Melting Point	Range: 272°C 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)

2.2 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 carbon dioxide 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 carbon dioxide for the compound of interest.

3. THERMODYNAMIC FRAME WORK

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:

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

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]:

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

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:

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

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:

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

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]:

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

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. In this work, the Peng-Robinson equation is utilized. The Peng-Robinson equation for a mixture is [Peng and Robinson 1976; Modell and Reid, 1983]:

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

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 (Equations 6 and 7) are utilized in this work.

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

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

$$\text{with: } a_{ij} = (1 - \delta_{ij}) \sqrt{a_i a_j} \quad \text{and } a_{ii} = a_i.$$

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:

$$a_i(\omega, T_r) = a(T_c) \alpha(\omega, T_r) \quad (9)$$

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

$$\alpha(\omega, T_r) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - \sqrt{T_r})\right]^2 \quad (11)$$

$$= \left[1 + \kappa(1 - \sqrt{T_r})\right]^2$$

$$b_i = \frac{0.07780 R T_c}{P_c} \quad (12)$$

The Peng-Robinson equation is often written in terms of the compressibility,

$$Z = (PV/RT):$$

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

where A and B are defined as:

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

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

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:

$$\ln(\hat{\phi}_i) = \frac{b_i}{b_M} (Z - 1) - \ln(Z - B)$$

$$+ \frac{A}{2\sqrt{2}B} \left(\frac{2 \sum_k y_k a_{ik}}{a_M} - \frac{b_i}{b_M} \right) \ln \left[\frac{Z + B(1 - \sqrt{2})}{Z + B(1 + \sqrt{2})} \right] \quad (16)$$

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., $y_i = P_i^{sat} / P$). 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 iteration is equal to the estimate at the start of the iteration to within some prescribed tolerance.

4. ESTIMATION OF CRITICAL AND OTHER REQUIRED THERMODYNAMIC PROPERTIES

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 as compared to RDX (Figure 2) or HMX (Figure 3), all three contain $-\text{NO}_2$ groups, individually attached to a ring $>\text{N}-$ group. Group contribution methods were used to estimate the necessary values. Table 3 shows the group decomposition for these three compounds.

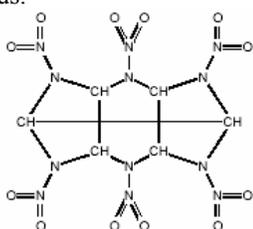


Fig. 1. Molecular Structure of CL20

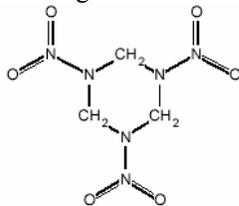


Fig. 2. Molecular Structure of RDX

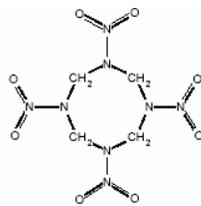


Fig. 3. Molecular Structure of HMX

Table 3. Group Decomposition of Energetic Molecules.

Group ID	CL20	RDX	HMX
	Number of Type	Number of Type	Number of Type
$>\text{N}-$ (ring)	6	3	4
$-\text{NO}_2$	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 $>\text{N}-$ (ring) group. For this group, the contributions to critical temperature and pressure were identical to those for a $>\text{N}-$ (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):

$$T_b = 198.2 + \sum_i n_i g_i \quad (17)$$

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

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

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

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

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.). This estimation technique requires the use of the normal boiling point, and thus, the values shown in Table 4 were used. Estimates for the critical temperature for the compounds of interest are shown in Table 5.

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 Temperature and Pressure

Compound	Critical Temperature, T_c Estimated using $T_b(\text{K})$	Critical Temperature, T_c Estimated using $T_b(\text{corr})$ (K)	Critical Pressure, P_c (bar)
RDX	965.4	842.7	58.0
HMX	1147.1	913.5	53.0
CL20	1483.6	1057.8	48.9

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. Estimates for the critical temperature for the compounds of interest are also shown in Table 5.

In addition to the critical properties (temperature and pressure), the acentric factor 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. (2000) recommend the estimation of the acentric factor using the three parameter Pitzer expansion:

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

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:

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

where T_{br} is the reduced normal boiling point and pressure is in bar. The functions, $f^{(0)}(T_{\text{br}})$, $f^{(1)}(T_{\text{br}})$, and $f^{(2)}(T_{\text{br}})$ 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) through (24) (Poling et al. 2000).

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

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

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

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:

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

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 6. 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).

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

where B is given by:

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

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 6.

Table 6. Estimated Acentric Factor

Compound	Acentric Factor (Estimated using Cranium)	Acentric Factor (Estimated using Eq. (22)-(25))	Acentric Factor (Estimated using Eq. (26)-(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 for CL20 were not identified through the literature search. Dionne et al. (1986) report the vapor pressure of RDX as

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

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):

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

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. (2000) recommend the use of the corresponding states method with the Ambrose-Walton expressions for the estimation of vapor pressure. The relevant expressions are:

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

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 6. 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 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 CO_2 , it is anticipated that the temperature range of interest is between approximately 35°C 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 CO_2 and are plotted in Figure 5.

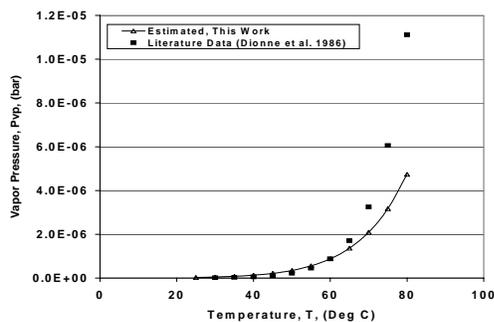


Fig. 4. Comparison of Estimated RDX Vapor Pressure with Literature Data.

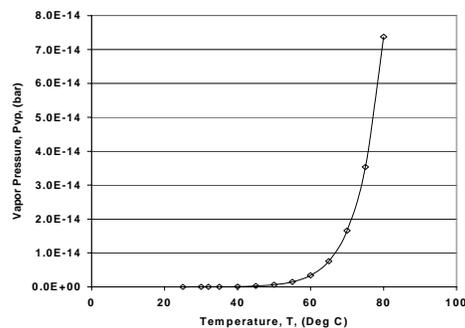


Fig. 5. Estimated Vapor Pressure for CL20.

5. VALIDATION OF THE DEVELOPED CODE

The Fortran code was validated using the solubility of naphthalene and of biphenyl in supercritical carbon dioxide. Data for these systems were measured by McHugh and Paulaitis (1980). For naphthalene in supercritical CO_2 , the value of the interaction parameter, δ_{12} , was set to 0.103, while for biphenyl in supercritical CO_2 , a value of 0.12 was used. These values for the interaction parameter were obtained by Schmitt (1984) by regression of the data of Tsekhanskaya 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 carbon dioxide (~ 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.

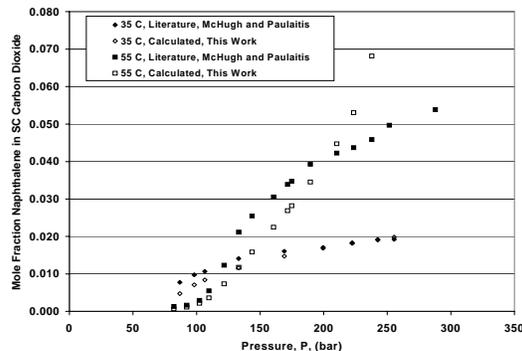


Fig. 6. Solubility of Naphthalene in Supercritical CO_2 - Comparison of Literature and Calculated Values.

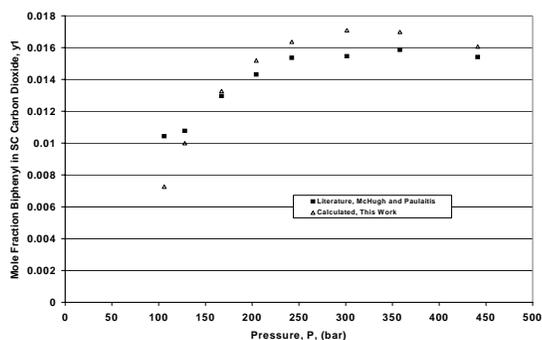


Fig. 7. Solubility of Biphenyl in Supercritical CO₂ Comparison of Literature Data and Calculated Values at 35.8°C

For biphenyl in supercritical carbon dioxide, the agreement between predicted values is much better. This 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 (carbon dioxide).

6. SOLUBILITY OF EXPLOSIVES IN SUPERCRITICAL CARBON DIOXIDE

6.1 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 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 were quite small, with magnitudes between 10⁻⁷ to 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 used. 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 carbon dioxide.

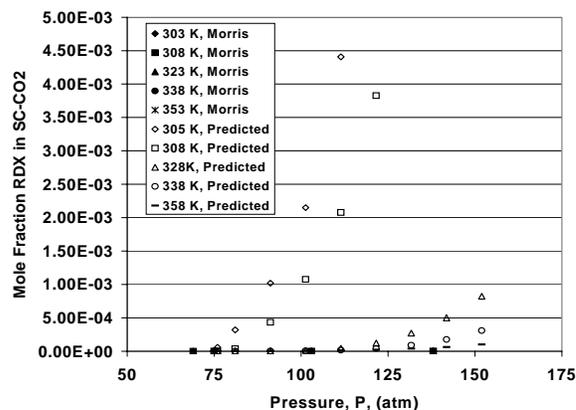


Fig. 8. Solubility of RDX in Subcritical and Supercritical Carbon Dioxide - Comparison of Predictions with Literature Data

6.2 SCF Predictions for CL20 in Supercritical CO₂

The solubility of CL20 in supercritical carbon dioxide 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 estimated of the coefficient B in equation (26). Since no experimental measurements were available, the initial estimate of the solubility was set to 1.0⁻¹⁶. Solubility was predicted over the temperature range of 305.15 to 368.15 K and over the pressure range of 74 to 150 atm. The temperature range corresponds to a range of reduced temperature of 1.003 to 1.21 with respect to carbon dioxide, 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).

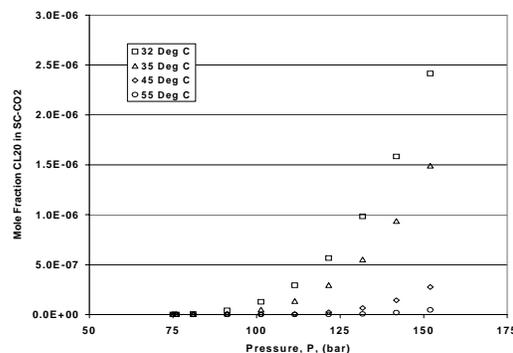


Fig. 9. Predicted Solubility of CL20 in Supercritical CO₂ - Low Temperature Range.

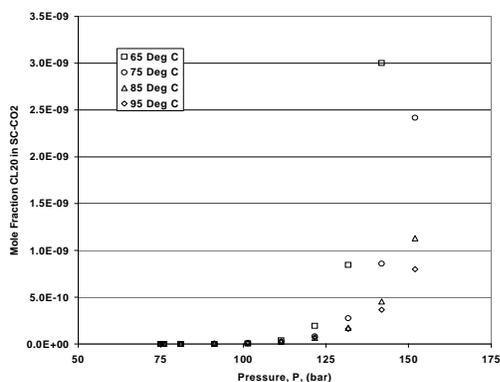


Fig. 10. Predicted Solubility of CL20 in Supercritical CO₂ - High Temperature Range.

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 carbon dioxide when compared to the behavior of naphthalene in supercritical carbon dioxide. 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 carbon dioxide, the influence of the supercritical fluid is stronger. It would be most desirable to operate in this region if one is interested in maximizing the solubility of the solute, CL20, in the carbon dioxide.

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 CL20 was accomplished using available group contribution techniques and property definitions. While CL20 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 CL20. All three species are comprised of similar molecular groups, the primary difference being the presence of -CH (ring) groups in CL20 and -CH₂ (ring) groups in RDX and HMX.

A Fortran code was developed for the estimation of the solubility of a solute in supercritical carbon dioxide. Performance of the code was validated using the data of McHugh and Paulaitis (1980) for naphthalene and biphenyl solubilities in supercritical carbon dioxide. The prediction of solubility for the explosive, RDX, in supercritical carbon dioxide was performed and the

predicted values compared to 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 CL20 in supercritical carbon dioxide, 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. The experimental measurement of the vapor pressure of CL20 should be performed. Second, the conditions that appear to be most viable for maximizing the solubility of CL20 in supercritical carbon dioxide are the lowest supercritical temperature examined (35°C) and the highest pressure.

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