AN ABSTRACT OF THE THESIS OF

Sarawadee Junsophonsri for the degree of Master of Science in Chemical Engineering presented on August 23, 1994.

Tittle: Solubility of Biocides in Pure and Modified Supercritical Carbon Dioxide.

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Abstract approved: _____

Keith L. Levien

A continuous flow apparatus was set up to determine the solubilities of biocides in pure and modified supercritical carbon dioxide (SC-CO_2). The reliability of the apparatus and the method were verified by measuring the solubility of phenol in SC-CO_2 and comparing it with literature data. The solubility of two biocides, TCMTB (2-[*Thiocyanomethylthio*]*benzothiazole*) and tebuconazole (α-[2-(4-*chlorophenyl*)*ethyl*]-α-(*1,1-dimethylethyl*)-*1H-1,2,4,-triazole-1-ethanol*) were determined in SC-CO_2 and modified SC-CO_2 at 50 and 65 °C and at selected pressures between 100 and 300 bar. Biocide solubilities increased significantly with pressure between 100 and 200 bar, but additional pressure produced only minimal increases in solubilities. A crossover point, the pressure at which the derivative of solubility with temperature changed from negative to positive, was observed for both biocides : 196 bar for TCMTB and 182 bar for tebuconazole. The solubility data for pure SC-CO_2 was correlated

using a density-based model and the Ziger and Eckert relationship. Linear relations were observed between the isothermal solubilities of biocides and the density of SC-CO_2 on a log-log scale. With the Ziger and Eckert model, the linear behavior of the isotherms collapsed into a single linear line. A maxima of 13.21 and 34.56 percent average absolute relative deviation (AARD) in mole fraction were observed for TCMTB and tebuconazole for the density-based model, respectively. And a maxima of 19.65 and 35.48 % AARD in mole fraction were observed for TCMTB and tebuconazole for the Ziger and Eckert model. The density-based model was a simple model used to describe temperature and pressure effects on solubility. The Ziger and Eckert model required more effect but provided temperature independent parameters which could have been found using only one set of isothermal data.

The effects of methanol or acetone as a cosolvent on the solubility of the two biocides were also studied. The presence of either cosolvent increased the solubility of tebuconazole, but had less effect on the solubility of TCMTB. At 5-10 mol % of cosolvent, solubility of either biocide increased with the amount of cosolvent used.

Solubility of Biocides in Pure and Modified Supercritical Carbon Dioxide

by

Sarawadee Junsophonsri

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NOMENCLATURE

a	=	van der Waals attractive parameter
[A]	=	Molar concentration of a solute in SCF, mol/lit
$[AB_k]$	=	Molar concentration of the solvato complex in SCF, mol/lit
b	=	van der Waals repulsive parameter
[B]	=	Molar concentration of solvent in SCF, mol/lit
Δe_i	=	Additive atomic and group contribution for the enegy of vaporization, cal/mol
E	=	Solubility enhancement factor ($=yP/P^{sat}$)
ΔE_v	=	Energy of vaporization
g	=	Constant in Equation 3.2-5 and 3.2-6
ΔH_{solv}	=	Heat of solvation
ΔH_{vap}	=	Heat of vaporization
ΔH	=	Total heat of reaction ($= \Delta H_{sol} + \Delta H_{vap}$)
k	=	Association number
K	=	Equilibrium constant
M	=	Molecular weight
P	=	Pressure, bar
q_v	=	Constant in Equation 3.2-7
q_s	=	Constant in Equation 3.2-4
q	=	Constant in Equation 3.2-8, 3.2-11 ($= q_v + q_s$)
R	=	Gas constant

NOMENCLATURE (Continued)

T	=	Temperature, K
Δv_i	=	Additive atomic and group contribution for molar volume, cm^3/mol
v	=	Molar volume, cm^3/mol
y	=	Mole fraction
w	=	Mass fraction

Greek symbols

α	=	Thermal expansion coefficient, K^{-1}
β	=	Constant in Equation 3.2-16 ($=\ln(M_A + kM_B) + q - \ln(M_B)$)
ρ	=	Density, g/cm^3
δ	=	Hildebrand solubility parameter, $(cal/cm^3)^{1/2}$
ε^*	=	Dimensionless energy parameter ($= \delta^2 v^L/2.303RT$)
ϕ	=	Fugacity coefficient
η_1	=	Slope parameter in Ziger and Ekert model
γ	=	Constant in Equation 3.2-16 ($=\Delta H/R$)
ϑ_2	=	Intercept parameter in Ziger and Ekert model
Δ	=	Ratio of solubility parameters ($= \delta_B/ \delta_A$)

NOMENCLATURE (Continued)

Subscripts

A	=	Heavy solute component (biocide)
B	=	Light solvent component (CO_2)
c	=	Critical point
g	=	Gas phase
liq	=	Liquid phase
r	=	Reduced properties

Superscripts

L	=	Liquid or subcooled liquid
s	=	Solid
sat	=	Saturated

SOLUBILITY OF BIOCIDES IN PURE AND MODIFIED SUPERCRITICAL CARBON DIOXIDE

Chapter 1

Introduction

1.1 Background

Supercritical fluids (SCFs) were discovered a century ago, but for the past two decades they have attracted interest due to the use of SCFs as solvents. The motivation for the development of SCF technology is a result of :

1) Environment problems associated with conventional organic solvents.
2) Conventional processes are often energy-intensive and the use of SCFs can reduce energy costs.
3) Increased performance demands for materials which traditional processing techniques cannot handles such as thermally sensitive materials.

A SCF is one that has been heated above its critical temperature (T_c) and compressed beyond its critical pressure (P_c). The P-T diagram and critical region of carbon dioxide are shown in Figure 1-1. It is possible to move directly from a liquid to a gas without phase separation simply by taking a path through the SCF region of the phase diagram (from point A to point B).

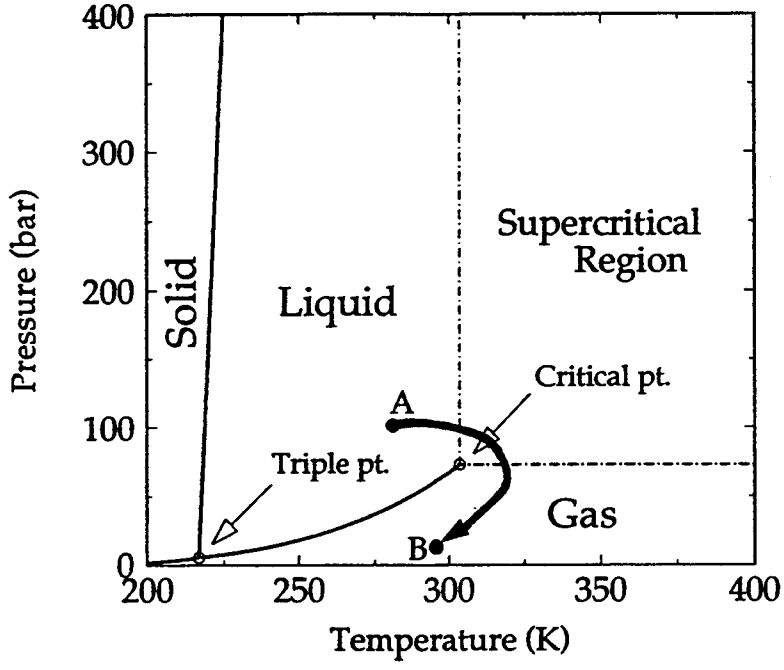


Figure 1-1 P-T Phase diagram for pure CO_2 (Angus et al., 1976).

By operating in the supercritical region, it is possible to take advantage of a variety of interesting and useful properties of SCFs. The density and solvent power of a SCF are like those of a liquid, while transport properties and compressibility are more like those of gas, as shown in Table 1-1. In the vicinity of the critical point, the solvent power of a SCF can be related to the solvent density (McHugh and Krukonis, 1986). Figure 1-2 shows the relationship between reduced pressure (P_r) and reduced density (ρ_r) for CO_2. The region of greatest interest is near the critical point $0.9<T_r<1.2$ and $1.0<Pr<3.0$, where T_r and P_r are the reduced temperature and pressure,

Table 1-1 Typical properties of a gas, liquid and supercritical fluid (Hoyer, 1985)

Property	Gas	SCF	Liquid
Density (g/cm^3)	$(0.6 - 2.0)\times10^{-3}$	0.2 - 0.9	0.6 - 1.6
Diffusion Coefficient (cm^2/sec)	0.1 - 0.4	$(0.2 - 0.7)\times10^{-3}$	$(0.2 - 2.0)\times10^{-5}$
Viscosity (cp)	$(1 - 3)\times10^{-2}$	$(1 - 9)\times10^{-2}$	0.2 - 3.0

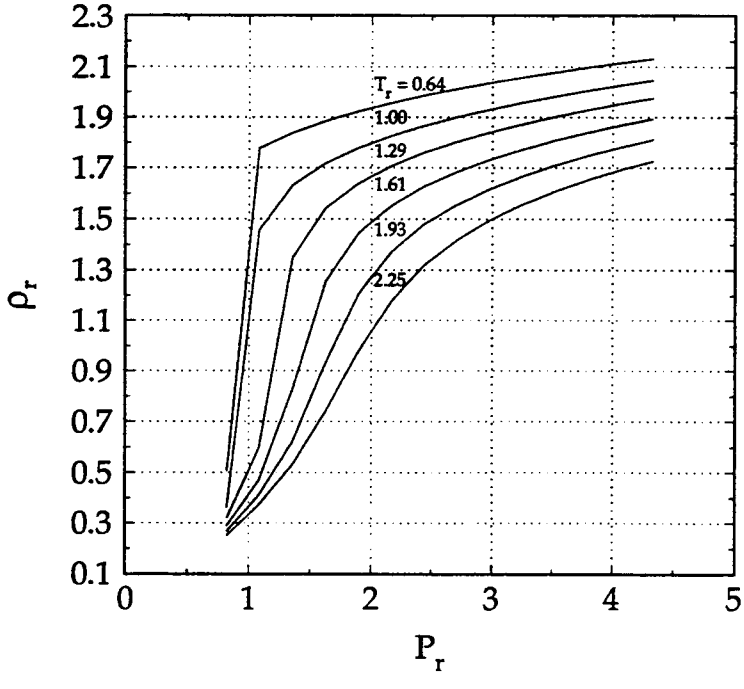


Figure 1-2 Reduced density *vs* reduced pressure for CO_2 using the modified BWR equation of state.

respectively. For CO_2, T_c = 304.1 K and P_c = 73.8 bar. In this region, relative small changes in temperature and pressure produce large changes in density, which makes the solvent power change drastically. SCF solvents penetrate substrates and approach equilibrium faster than normal liquids because they have higher diffusivity and lower viscosity than those of liquids. In addition, SCF solvents have little surface tension and thus no wetting problems.

SCFs have been used widely in many areas, mainly in extraction and separation. Deposition of materials in microporous substrates was one of the applications presented by Hoyer, (1985). Because the unique properties of SCFs allow them to penetrate into wood faster than liquids, SCF wood impregnation for preservation has been studied (Sahle-Demessie, 1994). However, the solubility data of biocides in pure and modified SC-CO_2 is critical to such a process and must be obtained for process development.

1.2 Review of Supercritical Solubility Studies

The most commonly reported solvent in solubility studies has been CO_2, which is attractive because of a convenient critical point of 304.1 K and 73.8 bar, low cost, nonflammibility and nontoxicity. Other interesting SCFs are water, methane, ethane, ethylene, fluoroform, etc. Solutes used generally fall into two classes : a series of simple hydrocarbons (mostly aromatic) or a selected variety of solutes of practical importance, ranging from coal tar to pharmaceutical products (Brennecke and Eckert, 1989). The investigation of

polar and nonpolar supercritical solvents to examine the effect of solvent size and polarity on solubilities has been reported (Hansen, 1985). The solutes were acridine, dibenzofuran, 9-fluorenone and carbon tetrachloride. The nonpolar solvents were CO_2, ethane, ethylene and sulfur hexafluoride and the polar solvent was fluoroform. The general conclusion was that solubility was dominated in most cases by dispersion forces and a polar solvent was a poor solvent for nonpolar compounds. In another solubility study, solutes were chosen to represent different chemical functionalities and solvents were supercritical CO_2, ethane, fluoroform, and chlorotrifluoromethane ($CClF_3$) (Schmitt and Reid, 1986 a). Solutes were either simple polycyclic hydrocarbons or monofunctional derivatives of these hydrocarbons, chosen on the basis of similar critical temperatures but greatly different structures. Ethane was the best solvent for the simple hydrocarbons. CO_2 was nearly as good, and both fluoroform and $CClF_3$ were poorer solvents for these solutes. Ethane and CO_2 were not as successful at dissolving more complex molecules, like 2-aminofluorene and 1,4-naphthoquinone. This confirmed that polar solvents are poor for simple nonpolar hydrocarbons, but show great potential for polar molecules and those containing functional groups that can be hydrogen bonded with the acidic proton of the solvent.

A study of three hydroxybenzene isomers in SC-CO_2 was also reported (Krukonis and Kurnik, 1985). The solubility was found to be a function of the melting point (or vapor pressure) of the isomer ; lower melting point

(corresponding to higher vapor pressure) indicated higher solubility. Thus a separation using a supercritical fluid could be done if there were significant differences in the isomer melting points (or vapor pressure).

Solubility of heavy organic solutes can be significantly increased by adding a cosolvent (entrainer) to the SCF solvent. A cosolvent has been described as a subcritical component added in relatively small amounts whose volatility is between those of the supercritical solvent and the solute (Bruner and Peter, 1981). The cosolvent is usually a common liquid solvent such as acetone, methanol, ethanol, water, toluene, carbon tetrachloride, hexane, etc. at a concentration less than 15 mol % (Schmitt and Reid, 1986 b). The purposes for using a cosolvent are (Bruner and Peter, 1981) :

1) To improve the solubility of a low volatility solute.

2) To modify P-V-T behavior of the supercritical solvent.

3) To improve selectivity when extracting a mixture while maintaining the sensivity of the solubility to small change in temperature and pressure.

Schmitt and Reid, (1986 b) studied the use of cosolvents in modifying the solubility of phenanthrene and benzoic acid in SC-CO_2 or SC-ethane. The cosolvents used in that study were acetone, benzene, methylene chloride and cyclohexane. They found that the solubility of both solutes increased with increasing amount of cosolvent, but the specific cosolvent used made little difference. Wong and Johnston, (1986) measured the solubilities of three

sterols of similar polarity : cholesterol, stigmasterol, and ergosterol. They found no improvement in solubility when a cosolvent was added to the SCF. These findings suggested that a cosolvent could facilitate separations if the solutes were of differing polarities (Dobbs et al., 1987). A mixture of solutes (naphthalene and benzoic acid) was studied by Kurnik and Reid, (1982). They found that the solubilities of these compounds in the ternary systems (SC-CO_2 + two solutes) were much greater than in the binary systems (SC-CO_2 + one solute), typically on the order 100 %. This finding suggests that one solute acts as a cosolvent for the other solute in the ternary system.

The solubility of a solute in an SCF is probably the most important property that must be determined and modeled in order to design an effective supercritical wood impregnation process. In particular, the pressure and temperature, and therefore, density dependence of solubility must be understood when determining operating conditions. There are two major experimental methods for measuring the solubilities of a solute in supercritical solvents : the static method (or equilibrium method) and the dynamic method (or flow method).

1.2.1 Static Method (Equilibrium Method)

In a static apparatus, a liquid or solid solute is placed in a high pressure vessel with the SCF, and the mixture is stirred for several hours to ensure equilibrium is reached. A representative static apparatus is shown in

Figure 1-3 (McHugh et al., 1984). The main component in this system was a high pressure view cell. This cell allowed for visual determination of the phases present at equilibrium. The CO_2 gas was compressed and delivered to a holding tank with V1 and V2 closed and the pressure inside the tank was measured. The amount of gas in the tank was determined from the gas density, calculated from measured temperature, pressure and volume of the tank. The gas was then passed to the view cell, which contained a known amount of solute. A pressure generator connected to the view cell was used to generate the desired pressure for the view cell. The amount of gas inside the view cell was determined by a mass balance around the view cell, line and holding tank. The view cell was maintained at a constant temperature and pressure. The cell contents were mixed by a magnetic stirring bar. The solubility of a solute in SC-CO_2 was then measured. The pressure of the solute-SC-CO_2 mixture was isothermally increased until all the solute was solubilized in the SC-CO_2. At this point, a clear single fluid phase was present in the view cell. The mixture was then decompressed until solute precipitated from the solution and two phases existed in the view cell. Thus, the true solubility point is in the pressure interval between the existence of a single phases or two phases. The solute was alternately solubilized and precipitated a number of times to better define the pressure interval to within approximately ±1% of the absolute pressure reading. The solubility in this interval is known from the amount of solute loaded into the view cell. Later

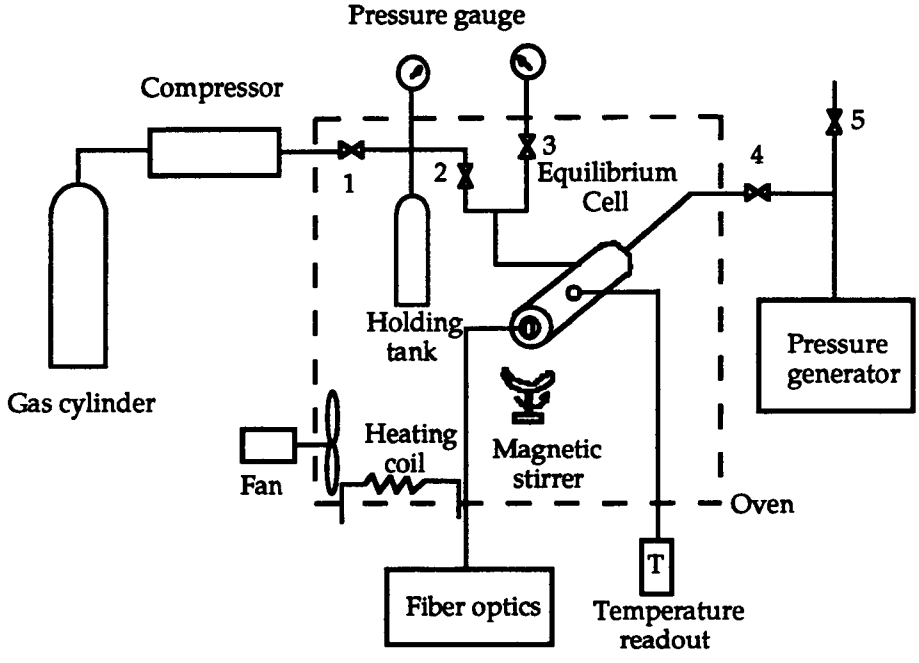


Figure 1-3 Schematic diagram of static method (McHugh et al., 1984)

some modifications were made to this design. A high pressure UV-vis cell will placed behind the equilibrium cell to monitor the solution density by the change in absorbance or transmittance of the solution (Robling and Frank, 1983). A sampling procedure was added to measure the composition of the solute in the heavier phase and the lighter phase (Katayama, 1975 ; Hsu et al, 1985; Lee and Kohn, 1969). Tsekhanskaya et al., (1962 and 1964) used a somewhat different technique to measure the solubility. A solid solute was first pressed into a pellet form and then weighed and placed inside a high pressure cell. Solvent gas at high pressure was introduced into the cell and the contents were allowed to attain equilibrium while being stirred. The equilibrium cell was depressurized causing the dissolved solid to deposit inside the cell and on the pellet. The precipitate was carefully brushed off the pellet and the pellet was reweighed. Thus, from a knowledge of weight loss of the pellet and the amount of solvent gas charged to the high pressure cell, the mole fraction of the solute was obtained.

The general advantages of the static method are :

1) The equilibrium phases are observed visually.

2) Minimum amount of solute and SCF are used in an experiment.

3) It can be used to measure equilibrium compositions of both coexisting phases.

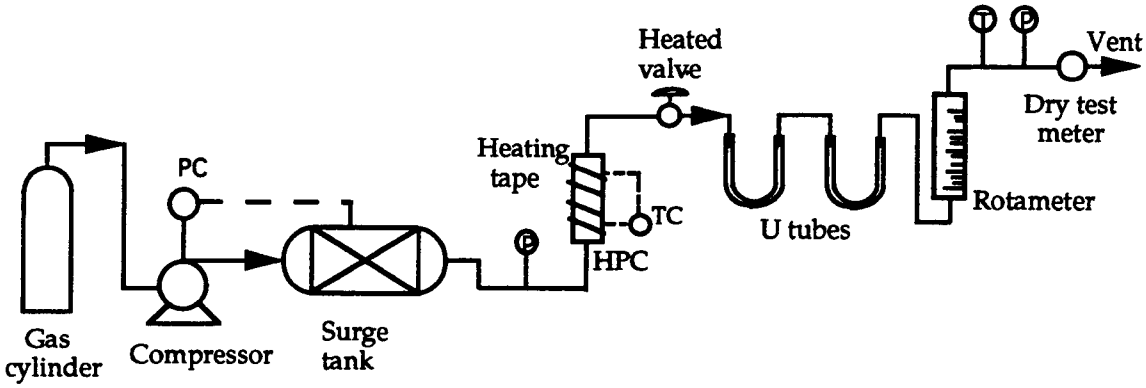
The general disadvantages of the static method are :

1) Time period required to reach equilibrium can be long.

2) When a sampling procedure is used, care must be taken that the system remains at equilibrium.

1.2.2 Dynamic Method (Flow Method)

In the dynamic method, equilibrium is obtained in a high pressure flow cell packed with a solute. In the high pressure cell the SCF contacts the condensed phase which is finely divided to provide a large surface area to reduce the contact time to reach saturation. A representative of this type of flow system is depicted schematically in Figure 1-4. This type of flow system has been widely used by many researchers (Kurnik et al., 1981; Johnston and Eckert, 1981; Van Leer and Paulaitis, 1980; Praunitz and Benson, 1959; Schmitt and Reid, 1984). The solvent fluid was supplied to a compressor from a pressure cylinder. Following the compressor was a surge tank, which minimized pulsations in pressure caused by the compressor. The fluid, at the desired pressure, then passed into the high pressure cell, where the solute was held, at an optimum flow rate to ensure equilibrium solubility was reached. The loaded SCF left the cell and was depressurized across a heated metering valve. The solute was collected in a cold trap, such as a U tube in an ice bath, and was measured either gravimetrically or using some appropriate analytical technique. The volume of the gas phase was monitored and recorded. The



TC - Temperature controller , PC - Pressure controller ,

T - Thermocouple , P - Pressure gauge

HPC - High pressure view cell

Figure 1-4 Schematic diagram of dynamic method. (Kurnik et al., 1981)

equilibrium solubility was calculated from the gas volume and the solute weight. The disadvantage of this procedure is the occurrence of valve clogging and solute hold up in the expansion valve. This problem has been solved by using a switching valve (McHugh and Paulaitis, 1980) as shown in Figure 1-5. The loaded SCF was sampled by switching the valve into a sampling position. When the loop is switched out of the system, the sample expanded into a transfer line. As a result of this expansion, the solute precipitated in the line. The volume of CO_2 in the loop was measured by displacing CO_2 gas into a tube filled with CO_2 saturated water at a known temperature. The precipitated solute was removed by flushing with a large amount of a suitable liquid organic solvent. The amount of solute was determined by a suitable analytical technique such as gas or liquid chromatography.

Adachi et al., (1984) used a similar sampling technique. Instead of a switching valve with a sampling loop, a sampling bomb was used.

In all dynamic methods, it is important to ensure that the solute and SCF solvent reach equilibrium. This is usually accomplished by making the measurement at a number of solvent flow rates. If the calculated solubility is independent of flow rate, equilibrium is usually assumed. The test must be performed for each system at each temperature studied.

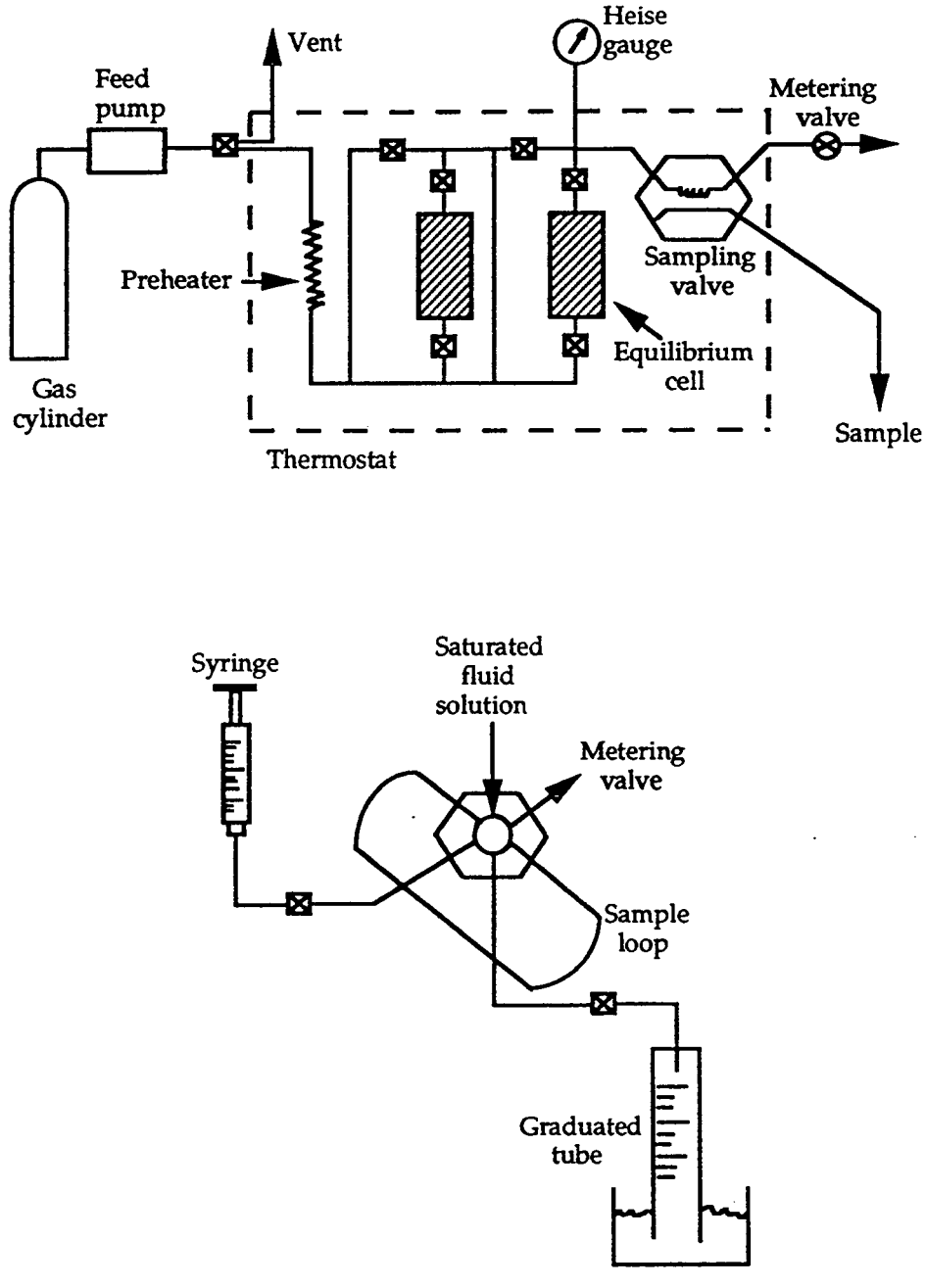


Figure 1-5 Schematic diagram of dynamic method with switching valve. (McHugh, 1984)

The general advantages of the dynamic method are :

1) Repeated measurements can be done rapidly.

2) Time required to reach equilibrium is less than with the static method.

3) The sampling procedure is simple and easy.

The disadvantages of the dynamic method are :

1) The equilibrium must be checked by looking for flow rate independence of the solubility measurements.

2) Because only the lighter phase is sampled, there is no way of knowing the solubility of the SCF in the heavier phase.

The apparatus used in this thesis was a single-pass flow system. The apparatus was similar to that used by Kurnik et al., (1981) without a surge tank. The details of the apparatus are described in Chapter 2.

1.3 Selection of SCF, Solutes and Cosolvents

The solvent chosen was CO_2 because it has a convenient critical temperature (304.1 K) and critical pressure (73.8 bar) which was used to operate at mild conditions and reduce the energy required. It is nonflammable and nontoxic which reduced environmental problems. It was readily available at high purity and inexpensive.

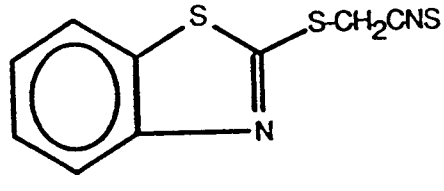
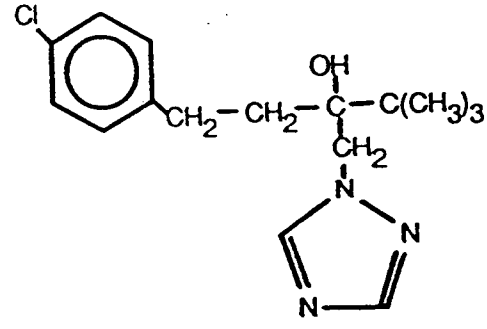
The model solutes chosen were TCMTB and tebuconazole, based on both experimental and practical reasons. First, both solutes displayed high

Table 1-2 Properties of biocides for solubility study

Biocide	Mol wt	State★	P^{vap} @ 20°C, (bar)	M.P. (°C)	δ* $(cal/cm^3)^{1/2}$
TCMTB	238.36	liquid	3.25×10^{-9}	35	12.99
tebuconazole	307.83	solid	7.2×10^{-12}	104	11.70

★ State at most conditions investigated in SC-CO_2 region.
* Estimated using atomic and group contribution method at 25 °C (Fedors, 1974), Appendix F.

Table 1-3 Molecular structure of biocides for solubility study

TCMTB	Tebuconazole
	

solubility in SC-CO_2 (greater than 2 weight %) based on previous solubility studies (Sahle-Demessie, 1994). Second, they are less dangerous biocides than current commercial preservatives. Third, they were available from the manufacturers at high concentrations. The properties of these biocides and the molecular structures are shown in Tables 1-2 and 1-3, respectively.

The model cosolvents selected were acetone and methanol, also based on both experimental and practical reasons. First, both cosolvents showed high retention time ratios in a cosolvent screening test using gas chromatography (Sahle-Demessie, 1994). Second, they are readily available at high purity and are inexpensive. Third, their properties are accurately known. The characteristics of these cosolvents are shown in Table 1-4.

1.4 Objectives

The objectives of this study can be divided into two categories : experimental and theoretical.

The experimental objectives were :

1) set up an experimental system which measures solubility of selected biocides in pure and modified CO_2.
2) verify the reliability of the solubility measurement system by reproducing known equilibrium data for phenol in SC-CO_2 at 60 °C.

Table 1-4 Properties of cosolvent used for solubility study (Lowry and Richardson, 1981)

Solvent	Type	Dipole moment μ debye[a]	Dielectric constant, ε at 25 ° C	Solubility Parameter, δ $(cal/cm^3)^{1/2}$	Polarizability $(cm^3 \times 10^{24})$
Acetone T_c = 508.1 K P_c = 47.0 bar MW = 58.08	Aprotic	2.9	20.70	9.6	6.41
Methanol T_c = 512.6 K P_c = 81.0 bar MW = 32.04	Protic	1.7	32.70	14.3	3.26

a From McClellan, 1974.

3) measure the solubility of TCMTB and tebuconazole in SC-CO_2 at 50 and 65 ° C and from 100 to 300 bar ($1.06<T_r<1.11$ and $1.36<P_r<4.07$).

4) measure effects of type and amount of cosolvent on solubility of biocides.

5) Evaluate feasibility of using this equipment to measure vapor pressure, e.g. for TCMTB using a gas saturation technique.

To make solubility data more useful, two correlation methods were applied to data for the binary systems (SC-CO_2 and biocide). Thus the theoretical objectives were :

1) correlate solubilities of biocides with density of SC-CO_2 using the density-based model derived by Chrastil, (1982).

2) correlate the solute enhancement factor, *E*, which is the ratio of measured solubility to that predicted from the ideal gas law, with a reduced solubility parameter expression, as derived by Ziger and Eckert, (1983).

Chapter 2

Experimental Procedure and Analysis

The experimental program was divided into two parts. The first part was to determine the solubility of each biocide and the second part was to measure the vapor pressure of TCMTB.

2.1 Solubility Measurements

2.1.1 Apparatus Description

The apparatus used in this study was a flow system show schematically in Figure 2-1. Liquid CO_2 from the cylinder was passed through the syringe pump (pump A, Isco model 260D), which was equipped with an external cooling jacket and a factory calibrated pressure transducer for maintaining constant pressure. The temperature of cooling water was maintained by a chiller (VWR Scientific 1156) at 4 °C to ensure that only liquid CO_2 existed in the pump. The pump was capable of delivering a constant flow rate ranging from 0.1 to 107.0 cm^3/min at a pressure up to 517.2 bar. In the case of using cosolvent along with CO_2, the cosolvent was introduced by using another syringe pump (pump B, Isco model 100D) which had delivery rates between 0.1 and 25.0 cm^3/min and pressure up to 689.7 bar. Liquid CO_2 and cosolvent were mixed and then compressed past the critical pressure of the mixture. The temperature of the mixture was raised

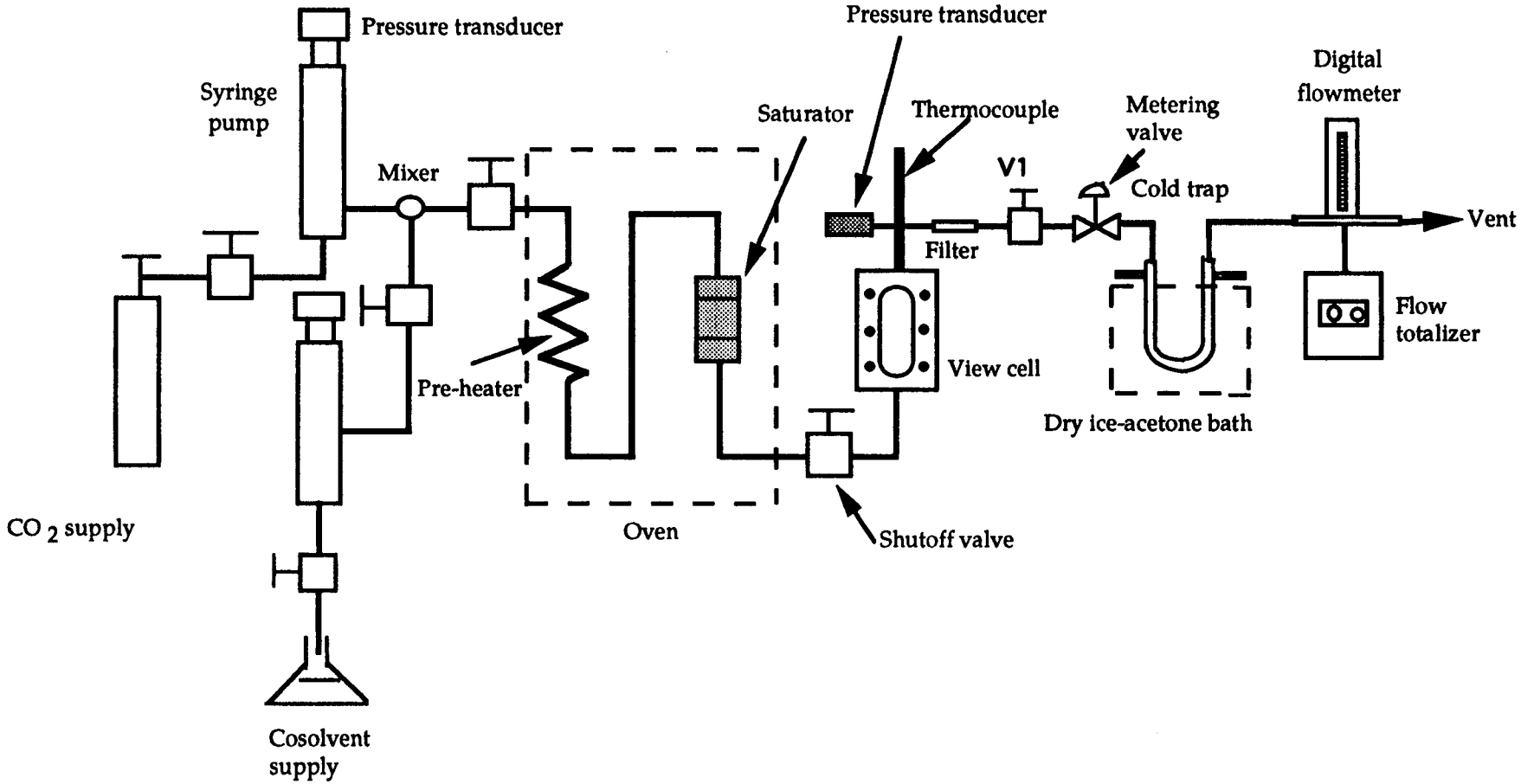


Figure 2-1 Schematic diagram of the experimental equipment for solubility studies.

by using a preheater to the desired value above the supercritical temperature of the mixture. The compressed fluid was then passed through a saturator packed with biocide. The preheater and the saturator were contained in an oven. The temperature of the oven was maintained within ± 1°C. In this study, the equilibrium cell consisted of the saturator, which was a 10 cm^3 stainless steel tube and a Jurguson view cell (Jurguson model 12-T-40 with a volume of 33.92 cm^3). The view cell was used to visually examine the two fluid phases and to ensure that there was no entrainment of biocide (heavy phase) and that the sampling was from the lighter phase. The saturator was filled with 80% by weight biocide and the remainder with filter paper and glass beads of 1.5 mm. diameter. This was done to increase the contact surface area between the supercritical fluid and the biocide. Glass wool was also inserted at the inlet and outlet of the cell to prevent entrainment of biocide. The Jurguson view cell was heated by a heating tape (Omega model FWH171-060) to the same temperature as the oven. A reducer, which had a 2-μm filter, was installed after the view cell to prevent entrainment of the biocides during the experiment. The equilibrium temperature and pressure of the system were measured at the exit of the view cell. The system pressure was measured with a pressure transducer and indicator (Heise model 901A). The system pressure was maintained constant to within ± 5% (Appendix A) of the desired value throughout the experiment. The temperature was measured with an accuracy of ± 0.1°C with a type T thermocouple and the temperature was regulated by a temperature controller (Omega CN9000A). The

loaded supercritical fluid was then routed through the valve, V1 (HP 15-11AF2) which was used to restrict the flow. Valve V1 was in series with a metering valve (Autoclave model 10VRMM-2812), which was used to set the flow rate of SCF. The flow rate was displayed on a digital flow meter. The temperature of valve V1 and all the lines outside the oven were heated to the temperature of the oven by a heating tape (Glas-col DETD256) controlled by a temperature controller (Fisher Scientific Type116). The micrometering valve and the line between the valves were heated to 20 - 30 °C above the melting point of the biocide by using heating tape (Glas-col DETD256) controlled by a temperature controller (Thermolyne CN45515) to reduce the Joule-Thompson cooling effect and minimize precipitation of the solute from solution. Precipitation is unavoidable due to the pressure drop, but heating helps reduced clogging of the valve. The deposited biocide and cosolvent were collected in a drying tube (Fisher Scientific 09-240B), which had glass wool at the outlet to prevent the entrainment of biocide. The drying tube was placed in the dry ice-acetone bath to ensure that all the biocide and cosolvent were precipitated inside the tube. The CO_2 gas was then passed through a flow meter (McMillan Co. model 310-3) and a flow totalizer (Kessler-Ellis Product Co. model INT96TBL1A), so that the total volume of the gas for the whole run period could be monitored. The collected samples were analyzed either by a gravimetric method using a precision balance (Mettler model B6) with precision ± 0.05 mg. or by using HPLC (High Pressure Liquid Chromatography, Shimadzu SCL6A).

2.1.2 Experimental Procedure

The temperature controller of the oven and the view cell were set to the desired value. The view cell reached thermal equilibrium after 90 minutes. The connection lines outside the oven were also heated with heating tape. The biocide was loaded inside the saturator and then heated for 30 minute to reach thermal equilibrium. Liquid CO_2 and cosolvent were mixed and compressed to the desired supercritical pressure. The supercritical mixture was then sent through the preheater to reach the required supercritical temperature and then sent on to fill the saturator. After 30 minute the valve to the view cell was opened and another 30 minutes period was used to equilibrate the entire system at the desired pressure. Prior to each experiment, the entire system was purged using loaded supercritical fluid for 60 minutes for TCMTB and at least 120 minutes for tebuconazole to achieve a smooth flow rate. This precaution was necessary to ensure that the equilibrium conditions within the high pressure cell were not disturbed. The biocide removed from this flushed sample was discarded. At this point the system was ready to be sampled. The flow rate of the gas was adjusted to approximately 200 cm^3/min. at ambient conditions using the micrometering valve. At any given temperature and pressure, three collection periods were performed. At 300 bar the collection period was 30 minute for TCMTB and 60 minutes for tebuconazole. At lower pressures the collection period was 60 minutes for TCMTB and at least 120 minutes for tebuconazole. Periods were larger for tebuconazole since its solubility is less

than that of TCMTB. The three measured solubilities were averaged to obtain the final equilibrium value. The standard deviation from the average was usually less than five percent.

This apparatus was similar to that used by Harcharan et al., (1990), without the surge tank to reduce pressure fluctuations. Fluctuation problems were eliminated by using piston pumps, which gave an even flow. The valve before the extractor was opened slowly to allow the fluid flow into the sample cartridge until the desired pressure was achieved.

2.1.3 Sample Analysis Procedure

2.1.3.1 Sample Analysis Procedure for TCMTB

There were two methods of analyzing the collected sample.

1) Gravimetric Method. This method was used when there was no cosolvent used. The drying tube was initially weighed at room conditions and then reweighed at the end of each run after allowing sufficient time to attain constant weight. Normally, the drying tube was left in the fume hood for at least 24 hours before weighing.

2) HPLC. This method was used when a cosolvent was used with TCMTB to avoid potential errors in the gravimetric method due to TCMTB's higher vapor pressure (than tebuconazole). The collected sample inside the tube was diluted in methanol to a known total volume of 50 cm^3 and 10 µl of this was

injected into the HPLC (Appendix B). The collected weight then was calculated by using a calibration curve for TCMTB (Appendix C).

2.1.3.2 Sample Analysis Procedure for Tebuconazole

The sampling procedure for tebuconazole was slightly modified since it could deposit as a solid inside the metering value. Plugging problems persisted even though the temperature of the micrometering value was kept 20-30 °C above the melting temperature of tebuconazole. Thus the sampling procedure was modified by flushing the tube behind the valve V1 in Figure 2-1 and the micrometering valve with methanol into a weighted beaker. The drying tube and the beaker were then left in the fume hood for at least 72 hours before reweighing. The amount of methanol used was between 20 and 25 cm^3. The collection and analysis method for TCMTB and tebuconazole are summarized in the Table 2-1.

2.1.4 Solute packing in the Saturator (Sample Cartridge)

A solute was mixed with glass bead and cut filter paper in the ratio 80% and 20% by weight and packed in the sample cartridge in an alternate layer as shown in Figure 2-2. Glass wool was inserted at the inlet and outlet to prevent the entrainment of solute. Metal frits were also used for the same purpose. For

Table 2-1 Summary of sample collection and analysis method

Solute	Solvent	Collection method	Analysis method
TCMTB	Pure CO_2	No flush*	Gravimetric
	CO_2 + cosolvent	No flush*	HPLC
tebuconazole	Pure CO_2	Flush**	Gravimetric
	CO_2 + cosolvent	Flush**	Gravimetric

* The line and the metering valve were not flushed by methanol.
** The line and the metering valve were flushed by methanol.

each run, 5 to 6 grams of solute were added to ensure that the system was saturated with solute.

2.1.5 System Test

In order to verify the reliability and efficiency of the solubility apparatus and the technique employed in this study, the solubility of phenol in SC-CO_2 was determined at 60 °C for selected pressures from 170 to 230 bar, as shown in Figure 2-3. The results from this work are in agreement with Van Leer and Paulaitis data (Van Leer and Paulaitis, 1980) within 2% so the apparatus and method were considered adequate to measure the solubility of the biocides.

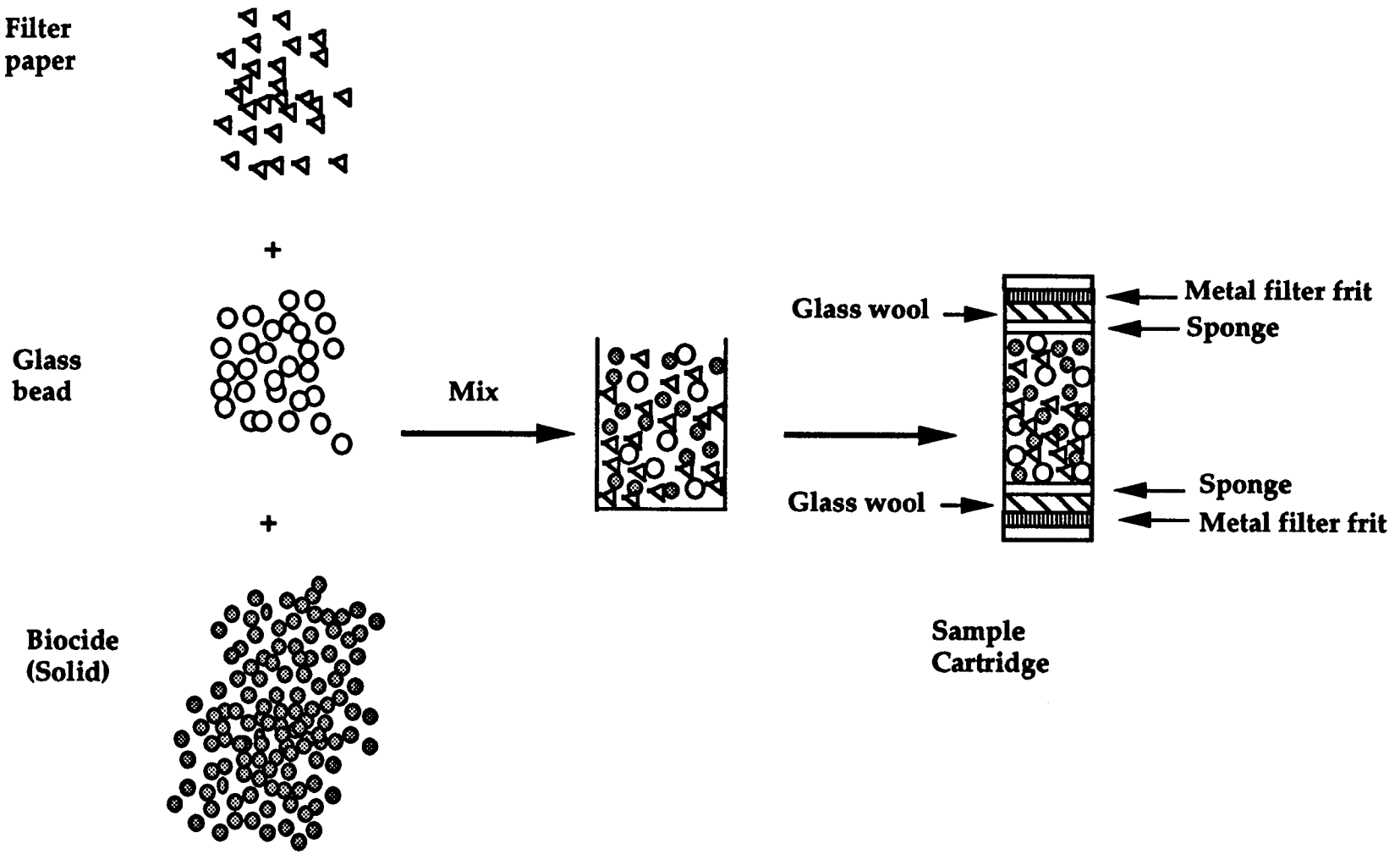


Figure 2-2 Sample preparation for solubility studies.

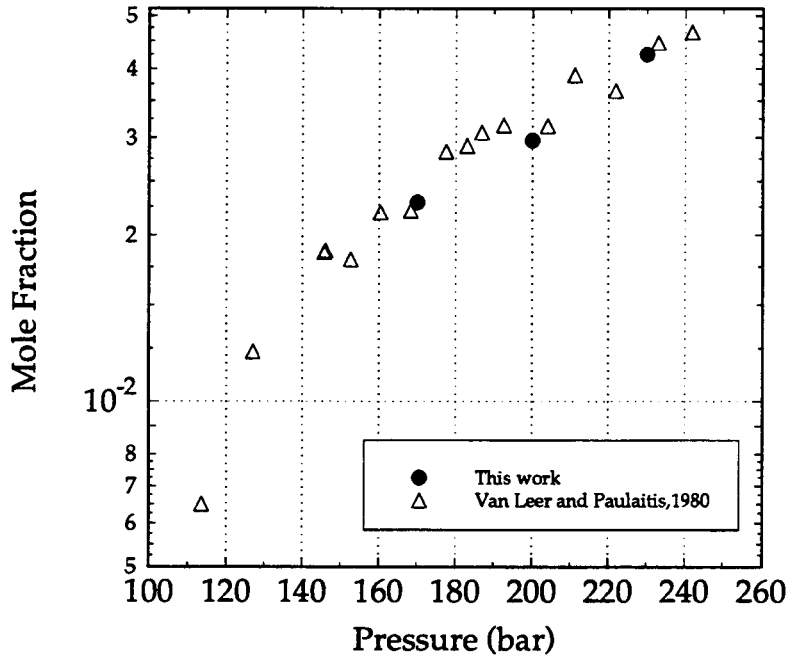


Figure 2-3 Solubility of phenol in supercritical carbon dioxide.

2.1.6 Calibration

The flow meter and flow totalizer were checked periodically for accuracy using a glass soap bubble meter.

2.1.7 Solute Change Over

After completing all runs for one biocide, the saturator was cleaned by soaking in ultrasonic cleaning solution (Fisher Scientific number 15-336-26) and

placed in a compact high performance ultra sonic cleaning system (Fisher Scientific model FS3) for 3 hours. A final soak in 30 cm^3 of acetone was done for 24 hours, followed by air drying. The view cell was flushed and rinsed several times with methanol (for tebuconazole) and acetone (for TCMTB), followed by an air flush until completely dry. The entire system was purged with 532 cm^3 (two syringe pump volumes) of SC-CO_2 at 300 bar and 50 °C to make sure that there is no residue of the previously used biocide.

2.1.8 Cosolvent Change Over

After completing all runs for one solvent, the system was depressurized and opened to remove the biocide in the saturator and the view cell. Then the entire system was purged with 266 cm^3 of SC-CO_2 (about one syringe pump volume) and with a mixture of SC-CO_2 and the new cosolvent at 300 bar and 50 °C for 3-4 hours to make sure that there was no residue of previously used cosolvent.

2.1.9 Establishment of Equilibrium

In order to check for mass transfer limits on measured solubility, the CO_2 gas flow rate was reduced from 500 to 70 cm^3/min for TCMTB at 300 bar and 50 °C. The results are presented in Table 2-2 and Figure 2-4. The measured solubility changed less than 1.3% for flow rates below 300 cm^3/min, which

indicated that equilibrium had been established at the exit of the high pressure cell. Since the solubility increased dramatically when the flow rate increased past 300 cm^3/min, an entrainment effect of the liquid biocide phase seems to have occurred. Thus the flow rate range of 200 to 300 cm^3/min was selected for all runs with TCMTB.

For tebuconazole in SC-CO_2, the flow rate effect was studied at 100, 200 and 300 cm^3/min at 200 bar and 50 °C. The results are shown in Table 2-3 and Figure 2-5. Since there was a different of less than 5 % in solubility measurements between 100 and 200 cm^3/min, the flow rate range of 100 to 200 cm^3/min was used for all runs with tebuconazole.

2.1.10 The Effect of Cold Trap

A dry ice-acetone bath was used to collect the precipitated biocide and cosolvent for all the experiments. Use of an ice in water bath was unacceptable because it failed to detect the effect of increased CO_2 flow rate to decrease the solubility of the impure (80.0 %) TCMTB, which was found using the colder bath as shown in Table 2-4.

Table 2-2 Effect of flow rate on solubility measurements of TCMTB at 50 °C and 300 bar

Flow rate (cm^3/min)	Solubility of TCMTB (weight fraction)$\times 10^4$	% difference between solubility
70	60.667	0 = base case
100	60.872	0.22
200	60.109	1.27
300	60.389	0.46
400	65.769	8.18
500	74.218	11.09

Table 2-3 Effect of flow rate on solubility measurements of tebuconazole at 50 °C and 200 bar

Flow rate (cm^3/min)	Solubility of tebuconazole (weight fraction)$\times 10^4$	% difference between solubility
100	23.283	0 = base case
200	24.273	4.07
300	21.555	12.60

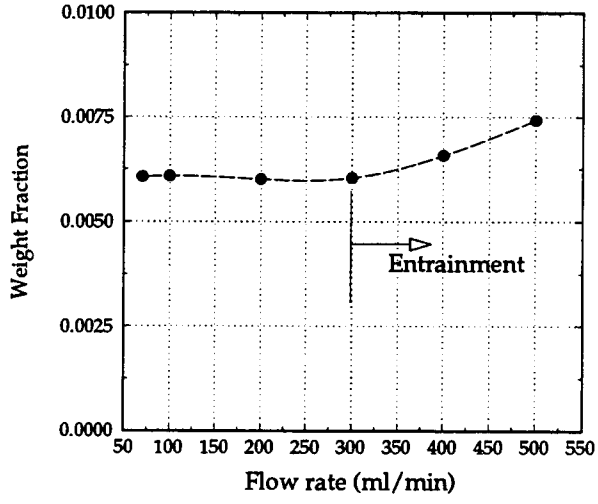


Figure 2-4 Flow rate effect for TCMTB in SC-CO_2 at 50 °C and 300 bar.

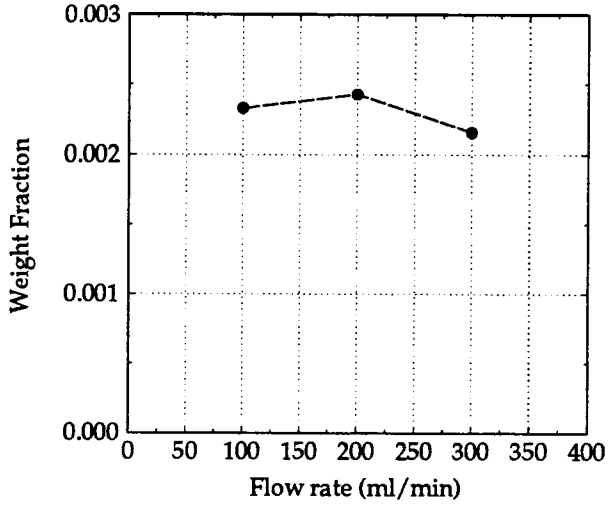


Figure 2-5 Flow rate effect for tebuconazole in SC-CO_2 at 50 °C and 200 bar.

Table 2-4 Effect of cold trap on measured solubility of 80.0% pure TCMTB in SC-CO_2 at 50°C and 250 bar using a gravimetric analysis

Flow rate (cm^3/min)	Solubility in ice bath (weight fraction)×10^4	Solubility in dry ice acetone bath (weight fraction)×10^4
200	65.01	80.71
300	65.27	73.77

2.1.11 Precaution in Sample Collection

To test whether any solute escaped from the drying tube, a second drying tube was placed downstream of the first tube with inserts of glass wool at the outlets of both tubes to prevent the entrainment of solute. The test run showed no significant accumulation of solute in the second tube at flow rates below 300 cm^3/min for tebuconazole under conditions of expected maximum solubility (300 bar and 65 °C). Therefore, only one drying tube was used in all subsequent runs.

2.1.12 Methanol Evaporation Check

Methanol was used as a liquid solvent to flush the precipitated tebuconazole from the drying tube and the metering valve. To confirm the

purity of methanol and check the weighing procedure, 25 cm^3 of methanol was poured into a preweighed beaker and allowed sufficient time to vaporize. The beaker was then reweighed and the weight change was measured. It was found that there was no weight change in this test and no nonvolatiles left in the beaker, therefore methanol was used without further purification.

2.1.13 Source and Purity of Chemicals

The source and purity of all chemicals used in this study are given in Table 2-5. All chemicals were used without further purification.

Table 2-5 Source and purity of chemicals

Chemical	Purity (%)	Company
TCMTB	80.0 or 99.6	BUCKMAN LABORATORIES , INC.
Tebuconazole	95.0	MOBAY CORP.
Phenol	99.0	FISHER SCIENTIFIC
Carbon dioxide	99.9	CARDOX, DIVISION OF AIRE LIQUIDE OF NORTH AMERICA
Acetone	99.7	MALLINKRODT SPECIAL CHEMICAL CO.
Methanol	99.9	MALLINKRODT SPECIAL CHEMICAL CO.

2.1.14 Melting Point Measurements

The melting points of TCMTB and tebuconazole were checked by using a capillary tube loaded with a sample and placed inside a magnetically stirred water or oil bath, respectively. The melting point occurred at 35 to 37 °C for TCMTB and at 104 to 107 °C for tebuconazole.

2.1.15 Carbon Dioxide Density Calculation

CO_2 density in this study was calculated using the modified BWR equation of state and was compared with tabulated density data (Angus, 1976). The error was found to be less that 0.2 %, even near the critical region. The program which was used to calculate CO_2 density using the modified BWR equation of state was written by Sahle-Demessie, (1994). The density value at 50 and 65 °C and ranging from 100 to 300 bar are shown in Appendix D.

2.2 Vapor Pressure Measurements

To verify the vapor pressure data supplied by Buckman Labs. Inc., a gas saturation technique was used to measure vapor pressure of TCMTB. The equipment used was the same as used in the solubility study, but nitrogen gas was used as the bulk fluid instead of SC-CO_2.

Experimental Procedure

The syringe pump was connected with a nitrogen cylinder. The pressure used was approximately 1.30 to 1.40 bar. Nitrogen was passed through the saturator, which was packed with TCMTB. A flow rate of 9 to 12 cm^3/min was used (Wong and Johnston., 1986). The necessary collection time used depends on the nature of the solute. For TCMTB, the collection time was approximately 6-8 hours using a dry ice-acetone cold trap. The collected sample was diluted with methanol to 25 cm^3 and this sample was analyzed by HPLC (Appendix B).

Chapter 3

Data Correlation Methods For Supercritical Solubility

3.1 Overview

Equations of state (EOS) models are useful to estimate solute solubility in a supercritical solvent, but they require not only the evaluation of solute critical parameters, which are often unavailable, but also the determination of temperature dependent solute-solvent interaction parameters associated with the use of mixing rules. Many EOS has been used to correlate solubility data with pressure and temperature based on fugacities, solubility parameters and virial coefficients. However, these equations usually do not describe the solubilities of different compounds in supercritical fluids over a wide range of pressures and temperatures. In many cases the estimation of the constants in these equations is difficult or impossible. In this work, two simple models were used to correlate the biocide-CO_2 equilibrium solubility data. First, an empirical log-log correlation between solute solubility and solvent density was used. This density-based model was first proposed by Chrastil, (1982) and later by Kumar and Johnston, (1988). Second, a semi-empirical semi-log correlation, based on the van der Waals equation of state and regular solution theory as proposed by Ziger and Eckert, (1983), was used.

3.2 Density-based Model

This model, Chrastil (1983), assumes that at equilibrium a solute molecule is associated with a fixed number of solvent molecules, resulting in the formation of a solvato complex. Chrastil stated, if one molecule of a solute, A, is associated with k molecules of a SCF, B, to form one molecule of solvato complex AB_k in equilibrium, the reaction can be written as follows:

$$A + kB \rightleftharpoons AB_k \tag{3.2-1}$$

From the law of mass action, an equilibrium constant, K, can be defined as :

$$K = \frac{[AB_k]}{[A][B]^k} \tag{3.2-2}$$

Using natural logarithms, Equation 3.2-2 can be rewritten as :

$$\ln [AB_k] = \ln K + \ln [A] + k \ln [B] \tag{3.2-3}$$

where [A], [B] and $[AB_k]$ are the equilibrium molar concentrations of the solute, the solvent and the solvato complex in a SCF solution, respectively and k is an association number. The temperature dependence of K, the equilibrium constant, can be expressed as:

$$\ln K = \frac{\Delta H_{solv}}{RT} + q_s \tag{3.2-4}$$

where ΔH_{solv} is the heat of solvation, and q_s is a constant. The molar concentration of solute [A] can be approximated using the Clausius-Clapeyron

equation and assuming an ideal gas equation of state :

$$\ln [P_A] = \frac{\Delta H_{vap}}{RT} + g \qquad (3.2\text{-}5)$$

where P_A is the partial pressure of solute A, ΔH_{vap} is the heat of vaporization of the solute, and g is a constant. From the ideal gas law, $P_A = [A]RT$, and when substituted into Equation 3.2-5, yields:

$$\ln [A] = \frac{\Delta H_{vap}}{RT} + g - \ln (RT) \qquad (3.2\text{-}6)$$

Since the change of term $\ln(RT)$ with temperature is small when compared to term $\Delta H_{vap}/RT$ the term $\ln(RT)$ can be combined with the constant g and Equation 3.2-7 is obtained.

$$\ln [A] = \frac{\Delta H_{vap}}{RT} + q_v \qquad (3.2\text{-}7)$$

where q_v is consider constant. Substitution of Equations 3.2-4 and 3.2-7 into Equation 3.2-3, yields:

$$\ln [AB_k] = \frac{\Delta H}{RT} + q + k \ln [B] \qquad (3.2\text{-}8)$$

where ΔH is the total reaction heat, $\Delta H = \Delta H_{sol} + \Delta H_{vap}$, and $q = q_s + q_v$. In order to express concentrations on a weight basis in g/lit, it is assumed that

$$[A] \leq [AB_k] \quad , \quad [AB_k] \approx \frac{c}{M_A + kM_B} \tag{3.2-9}$$

and

$$[B] \approx \frac{\rho}{M_B} \tag{3.2-10}$$

where c is the concentration of the solute in a SCF (g/lit), ρ is the density of pure solvent B (g/lit), and M_A and M_B are the molecular weights of the solute and of the solvent B, respectively. Since the presence of solute A in SCF solution is small when compared to solvent B, so the density of the SCF solution is assumed to be the density of solvent B. Substitutions for $[AB_k]$ and [B] in Equations 3.2-9 and 3.2-10, respectively, into Equation (3.2-8), led Chrastil to:

$$\ln c - \ln (M_A + kM_B) = \frac{\Delta H}{RT} + q + k \ln \rho - k \ln M_B \tag{3.2-11}$$

Equation (3.2-11) can be presented as :

$$c = \rho^k \exp (\frac{\gamma}{T} + \beta) \tag{3.2-12}$$

where

$$\gamma = \frac{\Delta H}{R} \tag{3.2-13}$$

and

$$\beta = \ln (M_A + kM_B) + q - k \ln (M_B) \quad \textbf{(3.2-14)}$$

Dilute concentrations of solute in SCF B can be expressed as weight fraction (kg of A/kg of B) and density can be expressed as kg/m^3 by dividing equation (3.2-12) by ρ, so the equation is obtained as :

$$w = \rho^{k-1} \exp \left(\frac{\gamma}{T} + \beta\right) \quad \textbf{(3.2-15)}$$

and the final equation is

$$\log w = (k-1) \log \rho + \frac{1}{2.303} \left(\frac{\gamma}{T} + \beta\right) \quad \textbf{(3.2-16)}$$

where w is the weight fraction of the solute in a SCF B and ρ is the density of a SCF B as kg/m^3. This expression was used to correlate the solubility data of this study.

Plots of the logarithm of the weight fraction of a nonpolar solute against the logarithm of supercritical solvent density have been found to be straight lines having a slope equal to k-1 and an intercept (where ρ =1) equals to $(\gamma/T + \beta)/2.303$ (Chrastil, 1982; Yun et al., 1991; Gurdial et al., 1989; Liong et al., 1992; Maheshwari et al., 1992). Values of γ and β were estimated from two isotherms. The association constant, k, expresses an average equilibrium association number, which is a characteristic constant for a given solvent and solute. The association number, k, was not expected to be an integer. In most cases solvato complexes were not stoichiometric because there are often

several, more or less stable, association complexes formed simultaneously. This density-based model was valid for solubility c less than 100-200 g/lit or w less than 0.1 kg/kg CO_2 (Chrastil, 1982). Solubilities of amino acids and sugar in SC-CO_2 were determined at pressure up to 2026.5 bar and a linear relation of log c *vs* log ρ was found in all cases (Stahl et al., 1978).

The density-based model has been widely used because it has several advantages over the traditional cubic equation of state. Chrastil, (1983) obtained straight and parallel lines which indicates that the number of molecules involved in the solvato complex is independent of both pressure and temperature. The values of the association constant, k, which were found to be nonintegers for a number of solid and liquid solutes in SC-CO_2 and ranged from 1.0 to 13.0. Liong et al., (1992) found that all of the esters studied gave straight but not parallel lines except for eicosatrienoic acid, where k values decreased with increasing temperature. They also found no relationship between the number of molecules involved in the solvato complex and the shape, size or type of the solute molecule. Yun et al., (1991) used this model to correlate the solubility data of cholesterol in SC-CO_2. They found the k value of cholesterol in SC-CO_2 was 6.88.

3.3 Ziger and Eckert Model

This correlation was derived by Ziger and Eckert in 1983 on the basis of the van der Waals EOS and regular solution theory. The van der Waals EOS

and mixing rules were used to evaluate the fugacity coefficient of the solute in supercritical fluid (SCF) phase in terms of solubility parameters for the solute and for the solvent.

The solubility of a solid solute in a SCF, as a function of operating pressure and temperature, was described by Prausnitz et al., (1986) as.

$$y_A = \frac{P_A^{sat}}{P\phi_A} \exp\left[\frac{v_A^s(P-P_A^{sat})}{RT}\right] \qquad \textbf{(3.3-1)}$$

The ratio of the observed solubility to the solubility based on ideal gas behavior of the SCF is defined as the enhancement factor, E :

$$E = \frac{y_A P}{P_A^{sat}} \qquad \textbf{(3.3-2)}$$

Equation (3.3-1) can then be written as :

$$\ln E = -\ln \phi_A + \left[\frac{v_A^s(P-P_A^{sat})}{RT}\right] \qquad \textbf{(3.3-3)}$$

Based on the van der Waals EOS, $\ln \phi_A$ for dilute mixtures is :

$$\ln \phi_A = \ln\left[\frac{v}{v-b}\right] + \frac{b}{v-b} - \frac{2(a_A a_B)^{\frac{1}{2}}}{vRT} - \ln z \qquad \textbf{(3.3-4)}$$

As stated by Giddings et al., (1969), the solubility parameter can be obtained using the van der Waals EOS as:

$$\delta_i = (a_i)^{\frac{1}{2}} \rho_i \qquad \textbf{(3.3-5)}$$

where a_i is the attraction parameter of the van der Waals EOS. If the solute is only slightly soluble, then the solution properties can assumed to be those of the pure solvent. Inserting equation (3.3-5) into equation (3.3-4) and assuming that $b_A \approx v_A^L$ and $a_{AB} = (a_A a_B)^{1/2}$, the following result was obtained:

$$\log \phi_A = \log \left(1+\frac{\delta_B^2}{P}\right) - \varepsilon_A^* \Delta(2 - \Delta) + \frac{v_A^L P}{2.303RT} \qquad \textbf{(3.3-6)}$$

where

$$\varepsilon_A^* = \frac{\delta_A^2 v_A^L}{2.303RT} \qquad \text{and} \qquad \Delta = \frac{\delta_B}{\delta_A}$$

δ_A and δ_B are the Hildebrand solubility parameters of the solute and solvent, respectively. Inserting equation (3.3-6) into equation (3.3-3) and assuming that the subcooled liquid volume is about that of the pure solid, leads to:

$$\log E = \varepsilon_A^* \Delta(2 - \Delta) - \log \left[1 + \frac{\delta_B^2}{P}\right] \qquad \textbf{(3.3-7)}$$

Equation (3.3-7) gives an approximate value for the enhancement factor. However, to account for the inadequacy of regular solution theory and the van der Waals EOS for highly asymmetric solute-SCF systems, two adjustable parameters were introduced by Ziger and Eckert, (1983). Their final recommended expression also replaced Δ by Δ/y_B to yield:

$$\log E = \eta_1 \left[\varepsilon_A^* \frac{\Delta}{y_B}\left(2 - \frac{\Delta}{y_B}\right) - \log \left(1 + \frac{\delta_B^2}{P}\right)\right] + \vartheta_2 \qquad \textbf{(3.3-8)}$$

where η_1 and ϑ_2 are the slope and intercept of the plot between log E and $[\varepsilon_A^* \Delta/y_B(2-\Delta/y_B) - \log (1+\delta_B^2/P)]$, respectively.

The Ziger and Eckert model has been used by many researchers (Yun et al., 1991; Gurdial and Foster 1991; Gurdial et al., 1989). Ziger and Eckert themselves have shown that for eleven nonpolar compounds in SC-CO_2 systems, the slope, η_1, was 0.497. Yun et al., (1991) found that the data of cholesterol and phenol in SC-CO_2 collapsed onto a line of slope 0.28. Since both compounds contained one -OH group in their molecular structure, the different value suggested that the slopes of the solubility isotherms obtained using the Ziger and Eckert model are dependent on functional groups in the solute. Gurdial et al. (1989, 1991) and Wells et al. (1990) have investigated the influence of functional groups on the value of η_1. They found a value 0.658 for carboxyl containing aromatic hydrocarbon-CO_2 system, such as benzoic acid and phenylacetic acid, compared with a slope of 0.42 which was observed for salicylic acid, which contains -CO_2H and -OH group in its structure. Thus, the presence of the highly polar -CO_2H functional group increased η_1, while -OH functional groups tended to decrease it. Gurdial et al. (1989) also found that the polarity of the solute (dipole moments varied from 0 to 4 debye) had little effect on Ziger and Eckert model parameters, since the same value of η_1 was obtained for eleven compounds, with the exception of benzoic acid. The polarity had some effect on density-based model parameters, which could be categorized based on the solute polarity. First, nearly parallel linear behavior

of solubility isotherms was found for low polarity compounds suggesting a single k value for those binary systems. Second, the moderate and high polarity compounds displayed solubility isotherms that were non-parallel straight lines or curved, suggesting the presence of nonstoichiometric solvato complex. These two models (Equation 3.2-16 and Equation 3.3-8) were used to correlate the binary data between solute and SC-CO_2 in this thesis.

The advantage of using these two models compared to EOS can be classified for each model as follow. The density-based model uses a smaller number of parameters that need to be evaluated and it has been found by others to be superior in its correlation over the range of experimental pressure and temperature (Liong et al. 1992). There are three major advantages of using the Ziger and Eckert correlation suggested by Gurdial and Foster (1991). Firstly, the use of the enhancement factor can incorporate known changes in vapor pressure into calculations and provides qualitative information about the solute-solvent interactions. Secondly, the introduction of the Hildebrand solubility parameter for the solute and solvent not only takes the size and the nature of the molecules into consideration but also accounts for the strength of solute-solute and solvent-solvent intermolecular forces (Barton, 1983). Finally, the use of temperature dependent solute and solvent solubility parameters within the independent variable can take the overall effect of system temperature into account in order to collapse individual solubility isotherms onto a single generalized line.

3.4 Calculation of Solubility Parameters

The solubility parameter has been defined as the square root of the internal pressure or the cohesive energy density (the energy associated with the net attractive interactions of the material, $-E_v/v$),

$$\delta = \left(\frac{\Delta E_v}{v}\right)^{\frac{1}{2}} \qquad (3.4\text{-}1)$$

where ΔE_v is the energy of vaporization and v is the molar volume of liquid. ΔE_v is in general a monotonically decreasing function of temperature which eventually becomes zero at the critical temperature, where the properties of saturated vapor and liquid become identical. On the other hand, the molar volume is a monotonically increasing function of the temperature. Since the cohesive energy is the ratio of these two, it must be a monotonically decreasing function of temperature with a maximum at 0 K and a value of zero at critical point.

At pressures below atmospheric pressure, that is at temperatures below the normal boiling point, the solubility parameter can be approximated by

$$\delta = \left[\frac{(\Delta H_{vap} - RT)}{v}\right]^{\frac{1}{2}} \qquad (3.4\text{-}2)$$

where ΔH_{vap} is the heat of vaporization of the liquid at temperature T. For dense gases the solubility parameter can not be related to the energy of vaporization, since vaporization can not occur under these conditions.

Giddings et al., (1969) have proposed an empirical correlation based on liquid chromatography studies. The following expression was obtained using van der Waals equation and assuming the equality of δ's for liquid state and for the dense gas at liquid densities

$$\delta = (1.25 P_C^{\frac{1}{2}}) \left[\frac{\rho_{r,gas}}{\rho_{r,liq}} \right] \qquad \textbf{(3.4-3)}$$

where δ is in calories per cubic centimeter, P_C is critical pressure in atmospheres and $\rho_{r,lig}$, the reduced density of liquids, is normally about 2.66. The first factor, 1.25 $P_C^{1/2}$, is associated with the chemical effect and the second term $\rho_{r,g}/\rho_{r,liq}$ is called the state effect. The important point of Equation 3.4-3 is that δ varies linearly with the gas density, which suggests that gas density is directly related to the solvent strength of the gas. For supercritical fluids, the maximum δ is obtained when P is at its largest possible value when T is barely in excess of T_C. The solubility parameter of CO_2 calculated by Equation 3.4-3 as a function of reduced pressure (P_r) and reduced temperature (T_r) is shown in Figure 3-1. Evaluation of solubility parameters and molar volumes of a solute were based on an atomic and group contribution approach (Fedors, 1974). For equation (3.4-1), Fedors assumed

$$\Delta E_V = \sum_i \Delta e_i \qquad , \qquad v = \sum_i \Delta v_i$$

where Δe_i and Δv_i are the additive atomic and group contribution for the energy of vaporization and molar volume, respectively, which have been

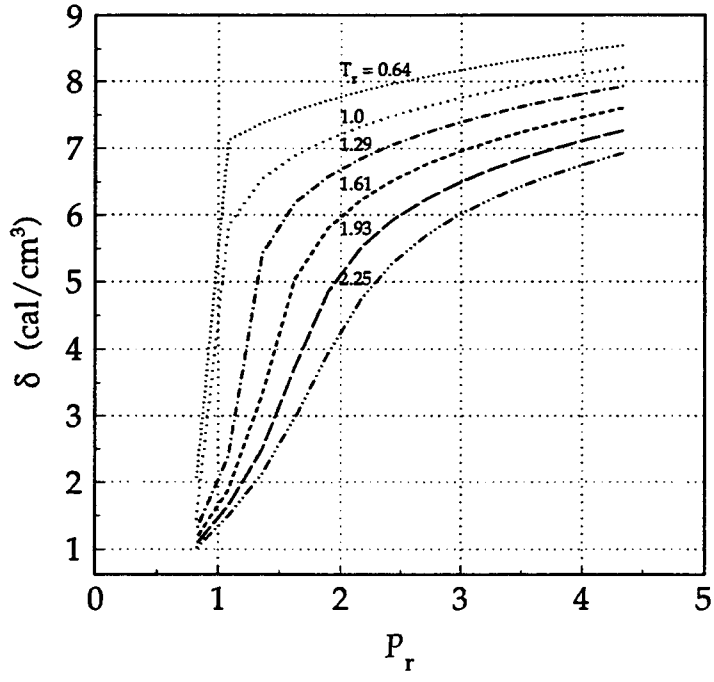


Figure 3-1 Solubility parameter *vs* reduced pressure for CO_2 (Giddings et al., 1969).

tabulated (Fedors, 1974; Barton, 1983). The solubility parameter of TCMTB and tebuconazole, as estimated using this method are presented in Appendix F. Fedors also provided a method to estimate the change in the solubility parameter for a temperature change of less than 50 K

$$\delta_2 = \delta_1[1 + 1.13\alpha(T_1 - T_2)] \qquad \textbf{(3.4-4)}$$

where δ_1 and δ_2 are the solubility parameter at temperature T_1 and T_2, respectively, and α is the thermal expansion coefficient. However, due to a

lack of experimental data, the thermal expansivity for any solute was assumed to be similar to the published value for naphthalene, $\alpha = 0.0007\ K^{-1}$(Vargaftik, 1975).

Chapter 4

Results and Discussions

4.1 Solubility Experimental Results

A continuous apparatus for measuring the solubility of biocides in pure and modified SC-CO_2 was set up as discussed in Chapter 2. Experimental solubilities of biocides in pure and modified SC-CO_2 has been measured. For each biocide, at each condition, 2 or 3 experimental solubility measurements were averaged (Appendix D). All standard deviations were less than 5 %, except at low pressure where solubilities of biocides in SCF were very low and sample preparation methods for HPLC analysis may have caused larger errors. The solubilities of biocide in pure SC-CO_2 and in mixture of cosolvent and SC-CO_2 systems are discussed separately in the following section.

4.1.1 Binary System (CO_2 + biocide)

The experimental equilibrium solubility data for TCMTB and tebuconazole in SC-CO_2 at 50 and 65 °C are plotted versus system pressure from 100 to 300 bar (Figures 4-1 and 4-2,respectively). Both TCMTB and tebuconazole show typical behavior of increased solubility with increased pressure. The crossover points for the two temperatures appear to be at approximately 196 and 182 bar, respectively. Below the crossover point, the

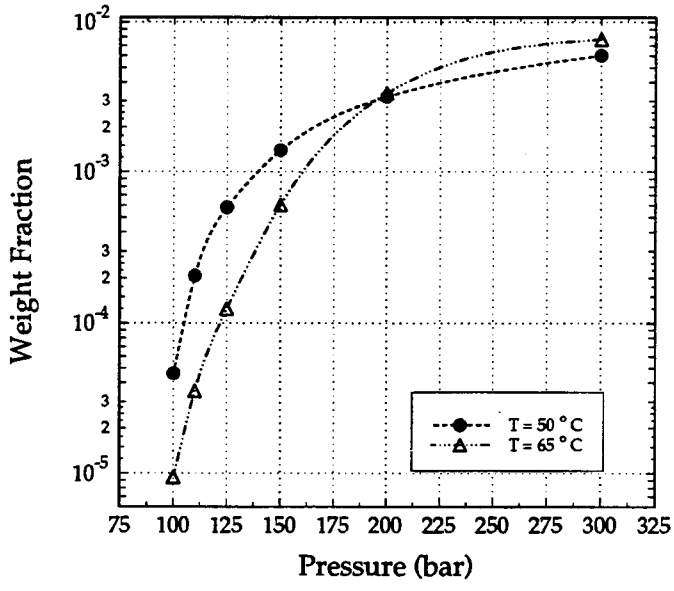


Figure 4-1 Solubility of TCMTB in SC-CO_2 as a function of pressure.

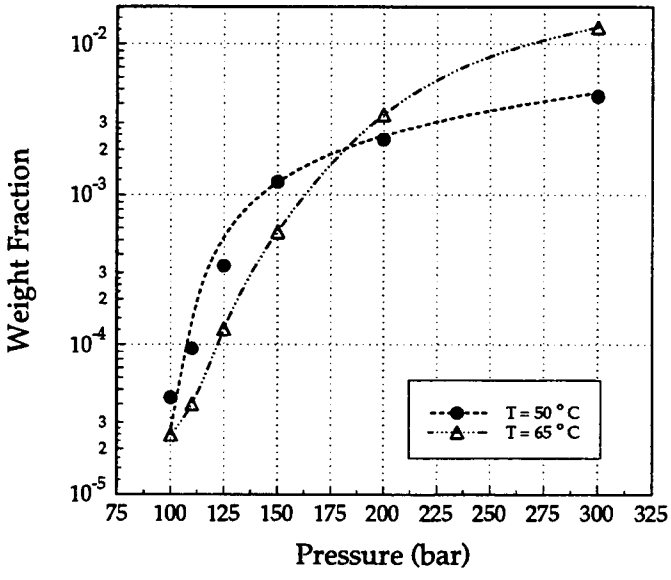


Figure 4-2 Solubility of tebuconazole in SC-CO_2 as a function of pressure.

solubility dropped as the temperature increased , a phenomena called retrograde vaporization. This was the result of the competing effects of temperature and density in the region where P_r is less than about 2.5. Raising the temperature increased the vapor pressure (which tends to increase the solubility), but also decreased the CO_2 density (which tends to lower the solubility). Below the crossover point the density effect dominated, and above the crossover point the vapor pressure effect dominated so increasing the temperature at high pressure increased the solubility. The logarithm of the experimental solubility data gave good linear correlations with pure CO_2 density (Figures 4-3 and 4-4). This was as shown by other workers (Chrastil, 1982; Kumar and Johnston, 1988; Gurdial et al., 1989; Liong et al., 1992). As expected, both showed higher solubility for higher temperatures at constant density. As the density of the fluid increases, the intermolecular mean free path decreases, increasing solute-solvent interaction and resulting in greater solubility. The solubility of TCMTB in SC-CO_2 is higher than that of tebuconazole. This can be explained because tebuconazole has a lower vapor pressure and higher molecular weight than TCMTB. The presence of the -OH functional group in tebuconazole molecules also hindered the solubility in SC-CO_2.

The solubility of the commercially used 80.0 % pure TCMTB in SC-CO_2 was also compared with 99.6% pure TCMTB (Figure 4-5). The error bars indicate the range of measured values of solubility. At high pressures the

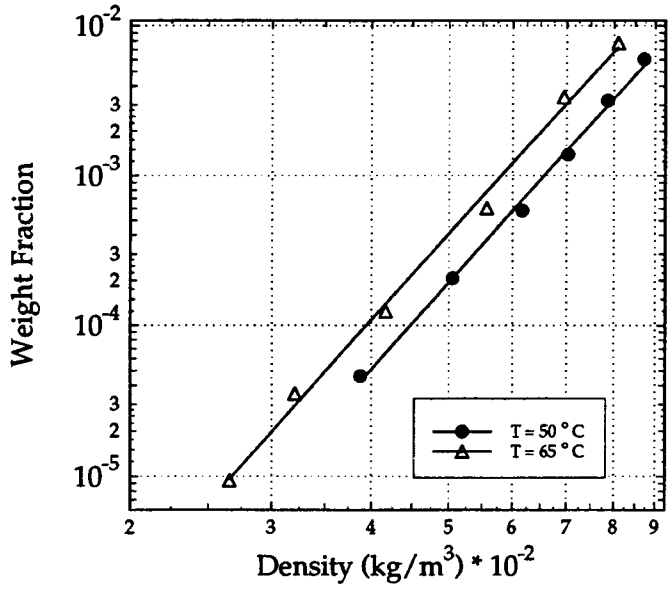


Figure 4-3 Log-log relationship between solubility of TCMTB and SC-CO_2 density.

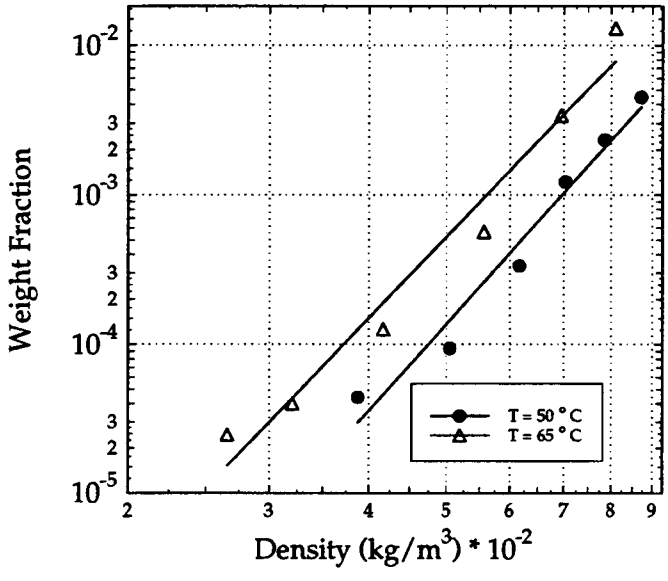


Figure 4-4 Log-log relationship between solubility of tebuconazole and SC-CO_2 density.

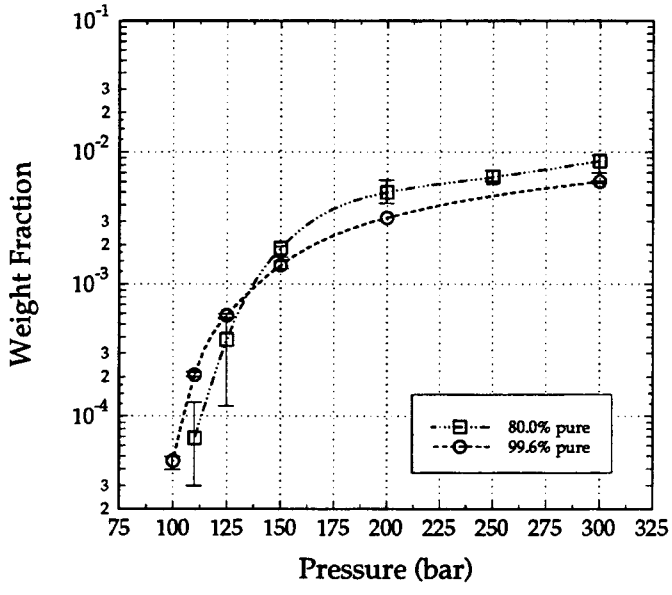


Figure 4-5 Solubility of 80.0 and 99.6% pure TCMTB in SC-CO_2 as a function of pressure.

lower purity sample had higher solubility while at low pressures the higher purity had higher solubility. These results may be explained in two ways. First, at high pressure the unknown inert ingredients may have higher solubility in SC-CO_2 than pure TCMTB. This would be considered a mixed solute in SCF, where the second solute increased the TCMTB solubility. Second, the 80.0% pure TCMTB container had two phases, solid and liquid, and only the liquid phase was used for the solubility study. The liquid sample of TCMTB may have had a component which acted as a cosolvent for TCMTB.

4.1.2 Ternary System (CO_2, cosolvent + biocide)

To study solubility of biocides in a modified solvent (CO_2 and cosolvent), all the experimental operating conditions were chosen to be at supercritical conditions compared to the critical loci of methanol-CO_2 and acetone-CO_2 systems (Figures 4-6, 4-7, 4-8 and 4-9). The solid circle points in the figures show the minimum experimental pressure and temperature used in this study. At the cosolvent concentrations used (3 mol % methanol or 1.68, 3 mol % acetone in CO_2), the mixtures were visually observed to exist as single phases.

The solubility data of TCMTB and tebuconazole in SC-CO_2 in the presence of a cosolvent are given in Appendix D. The plotted solubility data for TCMTB in 3 mol % methanol + SC-CO_2 or in 1.68 mol % acetone + SC-CO_2 versus pressure are presented in Figures 4-10 and 4-11, respectively. The solubility of tebuconazole in 3 mol % methanol + SC-CO_2 or in 3 mol % acetone + SC-CO_2 are similarly shown in Figures 4-12 and 4-13. Biocides in cosolvent + SC-CO_2 mixtures exhibited similar "crossover point" behavior to that seen in pure CO_2. The crossover pressures of tebuconazole in 3 mol % methanol or 3 mol % acetone were 232 and 207 bar, compared to 182 bar for SC-CO_2 alone. The crossover pressure of TCMTB in 3 mol % methanol was 245 compared to 196 bar for SC-CO_2 alone. In 1.68 mol % acetone, the crossover point was shifted to a pressure higher than 300 bar. Similar shifts of the crossover pressure have been observed by other researchers (Gurdial, 1992;

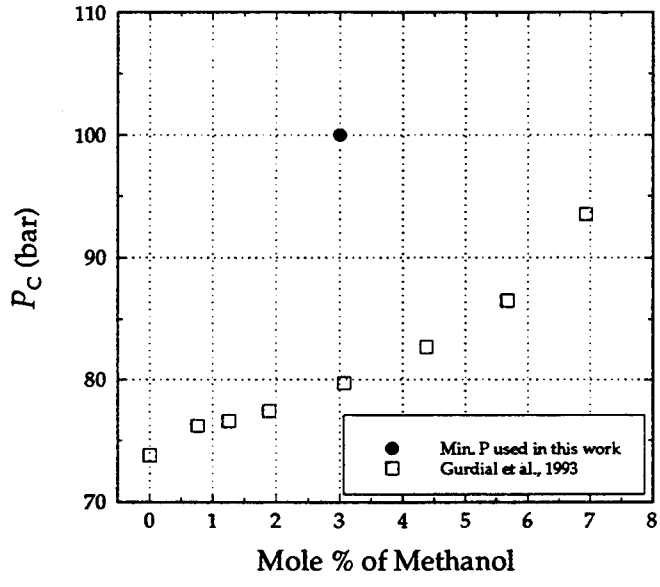


Figure 4-6 Critical pressure of CO_2 + methanol as a function of concentration.

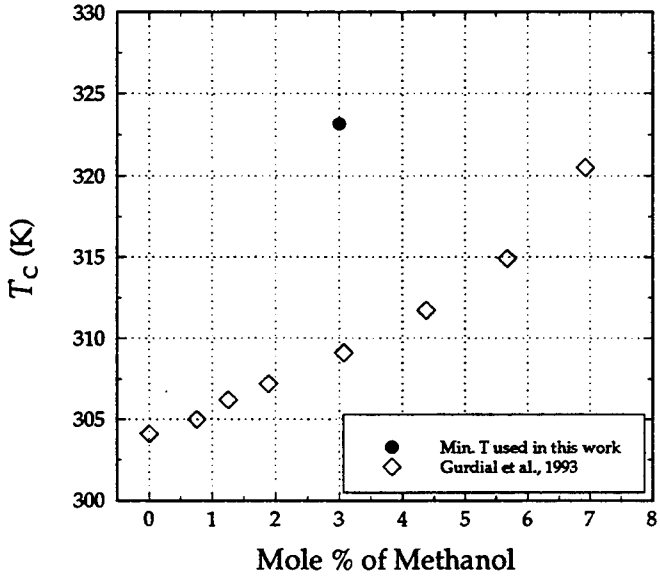


Figure 4-7 Critical temperature of CO_2 + methanol as a function of concentration.

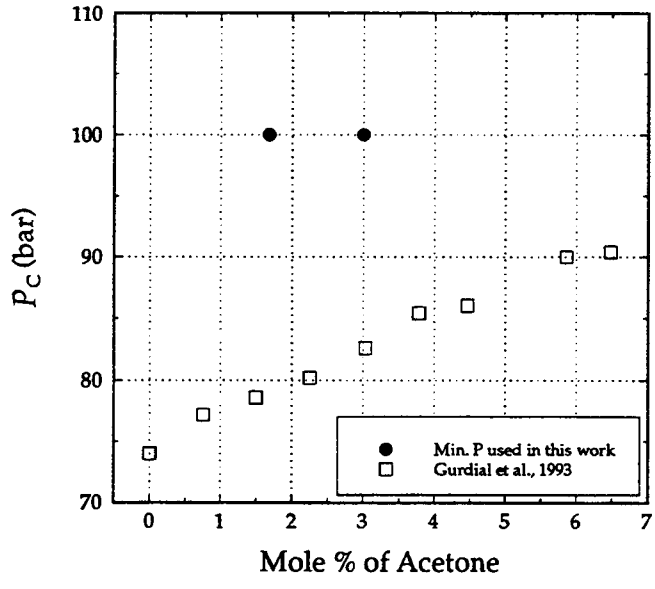


Figure 4-8 Critical pressure of CO_2 + acetone as a function of concentration.

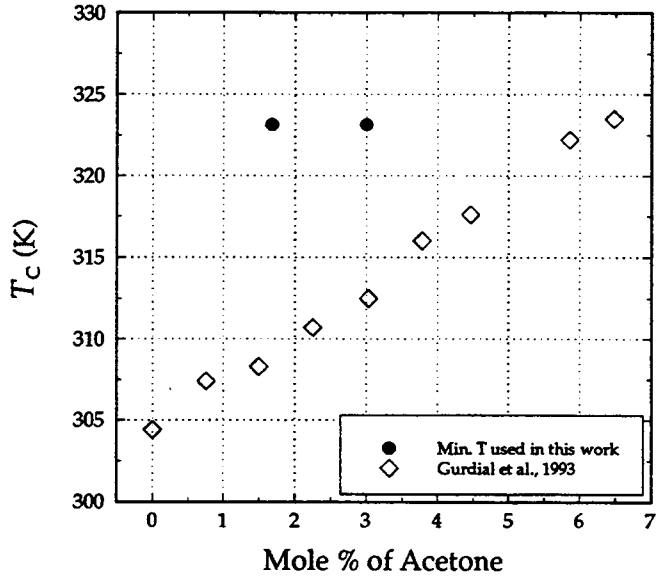


Figure 4-9 Critical temperature of CO_2 + acetone as a function of concentration.

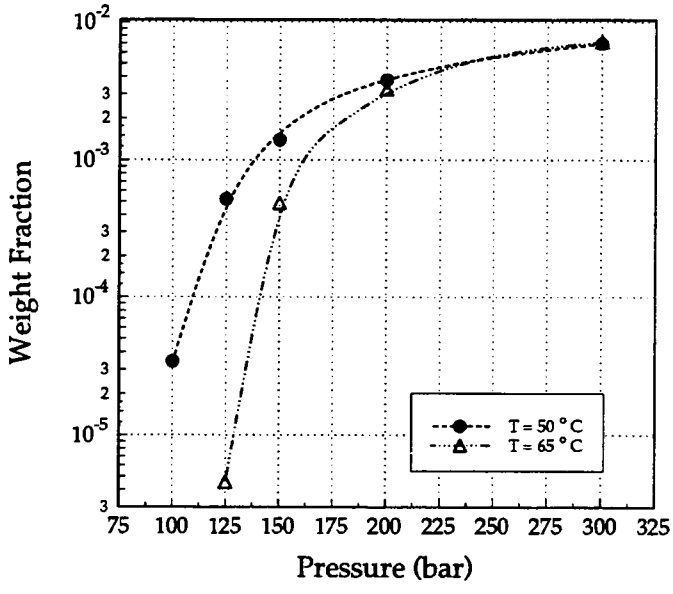


Figure 4-10 Solubility isotherms of TCMTB in 3 mol % methanol + SC-CO_2 as a function of pressure.

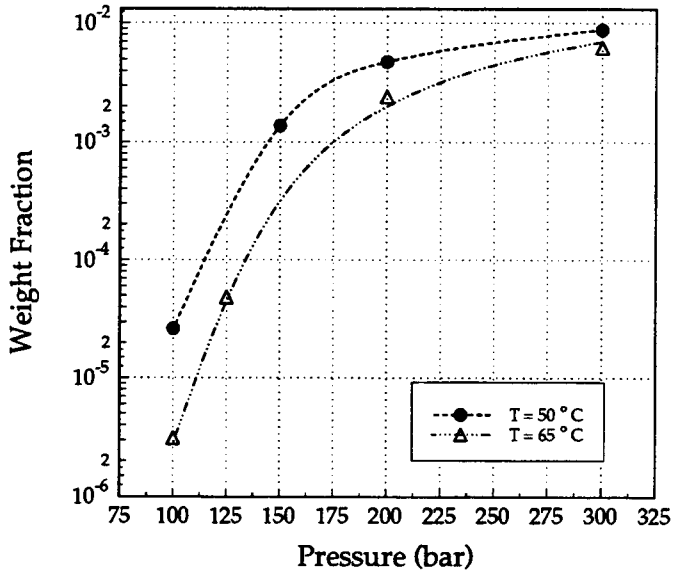


Figure 4-11 Solubility isotherms of TCMTB in 1.68 mol % acetone + SC-CO_2 as a function of pressure.

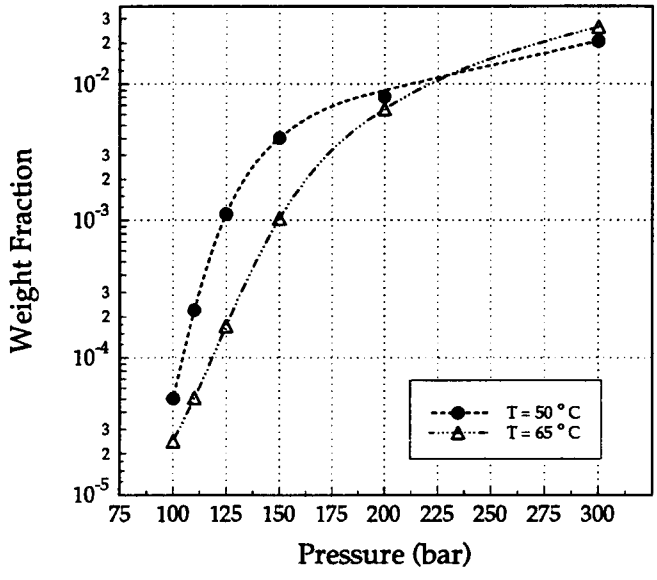


Figure 4-12 Solubility isotherms of tebuconazole in 3 mol % methanol + SC-CO_2 as a function of pressure.

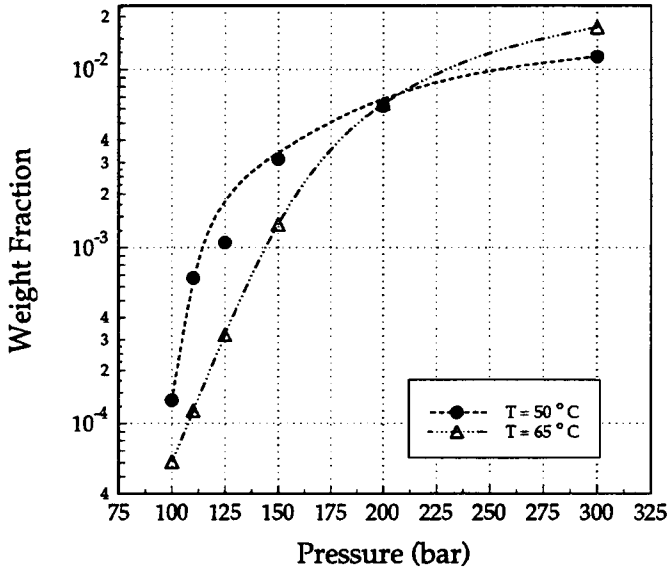


Figure 4-13 Solubility isotherms of tebuconazole in 3 mol % acetone + SC-CO_2 as a function of pressure.

Dobbs et al., 1986). Figure 4-14 is the plot of TCMTB solubility in SC-CO_2 and in 3 mol % methanol + SC-CO_2 at 50 °C. Figure 4-15 is a similar plot of tebuconazole solubility in SC-CO_2 and in 3 mol % acetone + SC-CO_2 at 50 °C. For TCMTB, methanol helped to increase solubility at high pressure, but at low pressure solubility was slightly less when methanol was present. For tebuconazole the presence of acetone helped to increase solubility at all pressures.

To highlight the solubility enhancement as a result of a cosolvent, the "cosolvent effect" is defined as the ratio of the solubility obtained with cosolvent to that obtained without cosolvent. Plots of the cosolvent effect as a function of system pressure are shown for TCMTB in Figures 4-16 and 4-17 and for tebuconazole in Figures 4-18 and 4 -19. Either cosolvent resulted in increased solubility of tebuconazole but neither had as large an effect for TCMTB. The influence of pressure on the cosolvent effect for TCMTB in methanol + SC-CO_2 and acetone + SC-CO_2 were similar. In both cases the cosolvent effect increased slightly with an increase in pressure. However, for tebuconazole, the changes in cosolvent effect due to increased pressure were different for the two cosolvents. The cosolvent effect increased monotonically with pressure for methanol + SC-CO_2 mixture at temperatures of 50 or 65 °C. However, the cosolvent effect exhibited a maximum at about 110 bar in acetone + SC-CO_2 for both temperatures. Cosolvent effect is lower at higher temperatures because the increase vapor pressure aids solubility in pure SC-

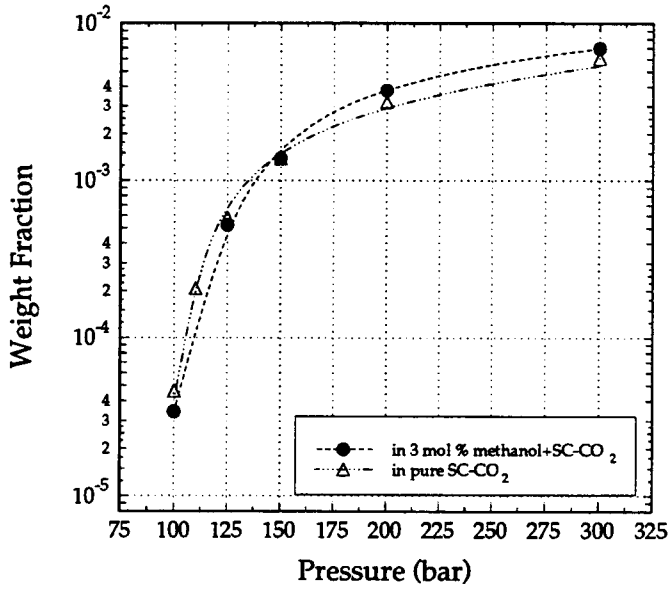


Figure 4-14 Solubility of TCMTB in pure and modified SC-CO_2 at 50 °C.

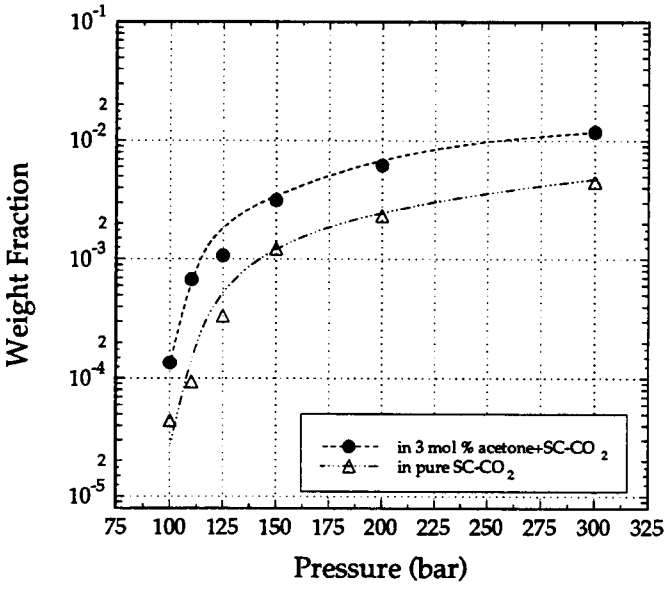


Figure 4-15 Solubility of tebuconazole in pure and modified SC-CO_2 at 50 °C.

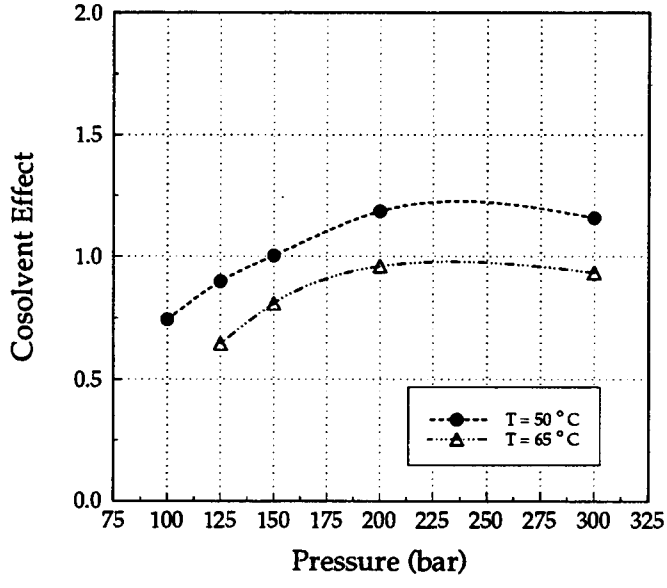


Figure 4-16 Cosolvent effect for TCMTB in 3 mol % methanol + SC-CO_2 as a function of pressure.

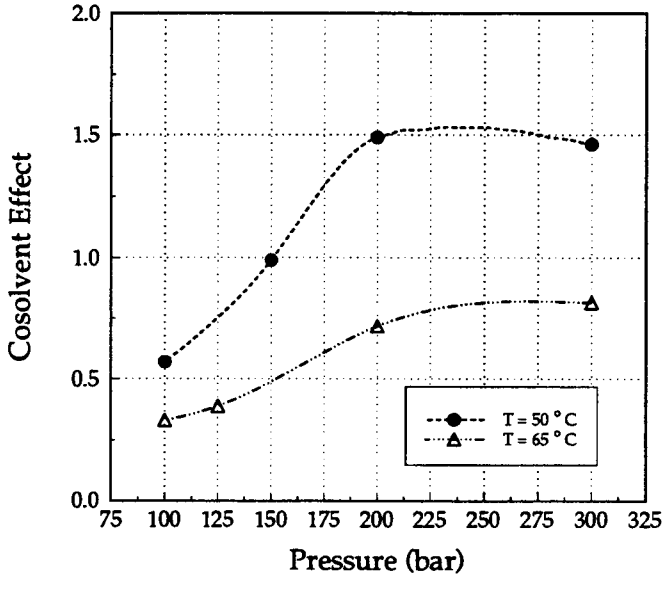


Figure 4-17 Cosolvent effect for TCMTB in 1.68 mol % acetone + SC-CO_2 as a function of pressure.

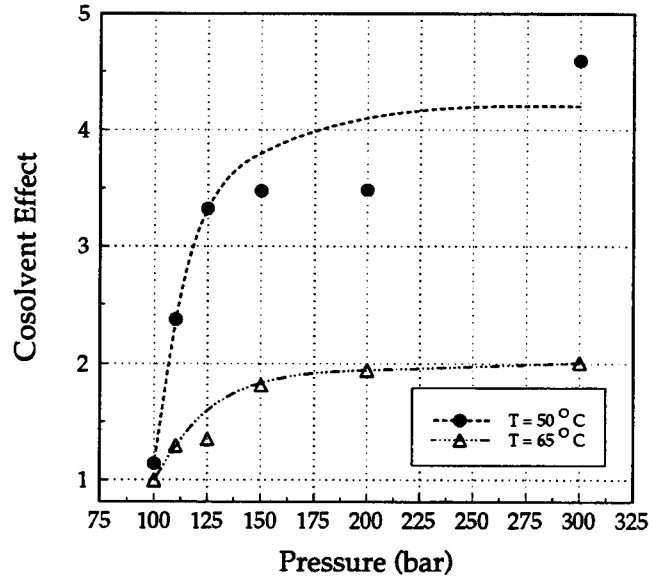


Figure 4-18 Cosolvent effect for tebuconazole in 3 mol % methanol + SC-CO_2 as a function of pressure.

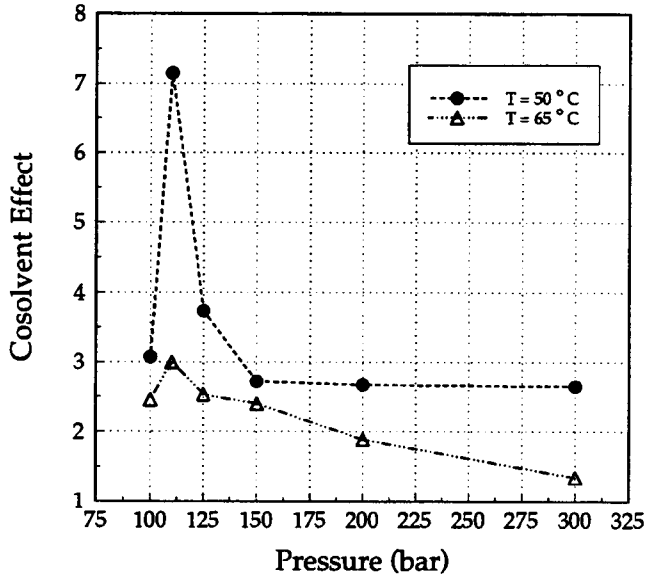


Figure 4-19 Cosolvent effect for tebuconazole in 3 mol % acetone + SC-CO_2 as a function of pressure.

CO_2 even more than in cosolvent mixtures, where chemical interactions increase solubility as well.

Similar results have been reported for the naproxen-methanol-CO_2 system (Ting et al., 1993). For 1.75 mol % methanol + SC-CO_2 mixture (low concentration of cosolvent), the cosolvent effect on naproxen showed only small increases with increases in pressure. For 3.5 mol % of methanol, the cosolvent effect had a maximum value at 138 bar. At a higher cosolvent amount of 5.25 mol % methanol the cosolvent effect monotonically decreased with pressure (Figure 4-20). This has been explained in investigations of the nature of the solute-cosolvent interaction under different conditions (Kim and Johnston, 1987 a, 1987 b; Yonker and Smith, 1988, 1989; Knutson et al., 1992) using U-V visible or fluorescence spectroscopy. Those authors showed that the region near the solute molecule was enriched with cosolvent molecules so that the local concentration of cosolvent near a solute molecule was several times higher than that of the bulk concentration. Such local ordering of the cosolvent molecules, however decreased with increasing pressure, and at high enough pressures the concentration of the cosolvent around the solute approached the bulk concentration. While the local composition enhancement (which is the ratio of local concentration of cosolvent molecule around the solute molecules to bulk concentration) decreases with pressure, the absolute local concentration of cosolvent around the solute will always increase with increasing pressure, due to the increase in density, as illustrated in Figure 4-21.

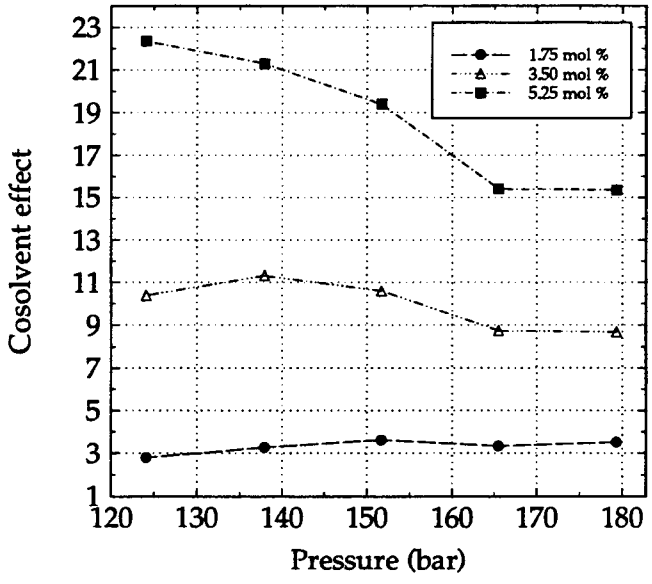


Figure 4-20 Cosolvent effect for naproxen in methanol + SC-CO_2 at 60 °C (Ting et al., 1993).

Both local composition enhancement and absolute local concentration of cosolvent around the solute can be used to explain the change in cosolvent effect with system pressure. At low cosolvent concentration, the cosolvent effect depends predominantly on the absolute concentration of cosolvent around the solute. As pressure increases, the absolute concentration increase causes the cosolvent effect to increase. At high cosolvent concentration, the effect of local composition enhancement becomes significant. The local composition enhancement is maximum in the region of high compressibility (near P_c) therefore it is possible that a decrease in local composition

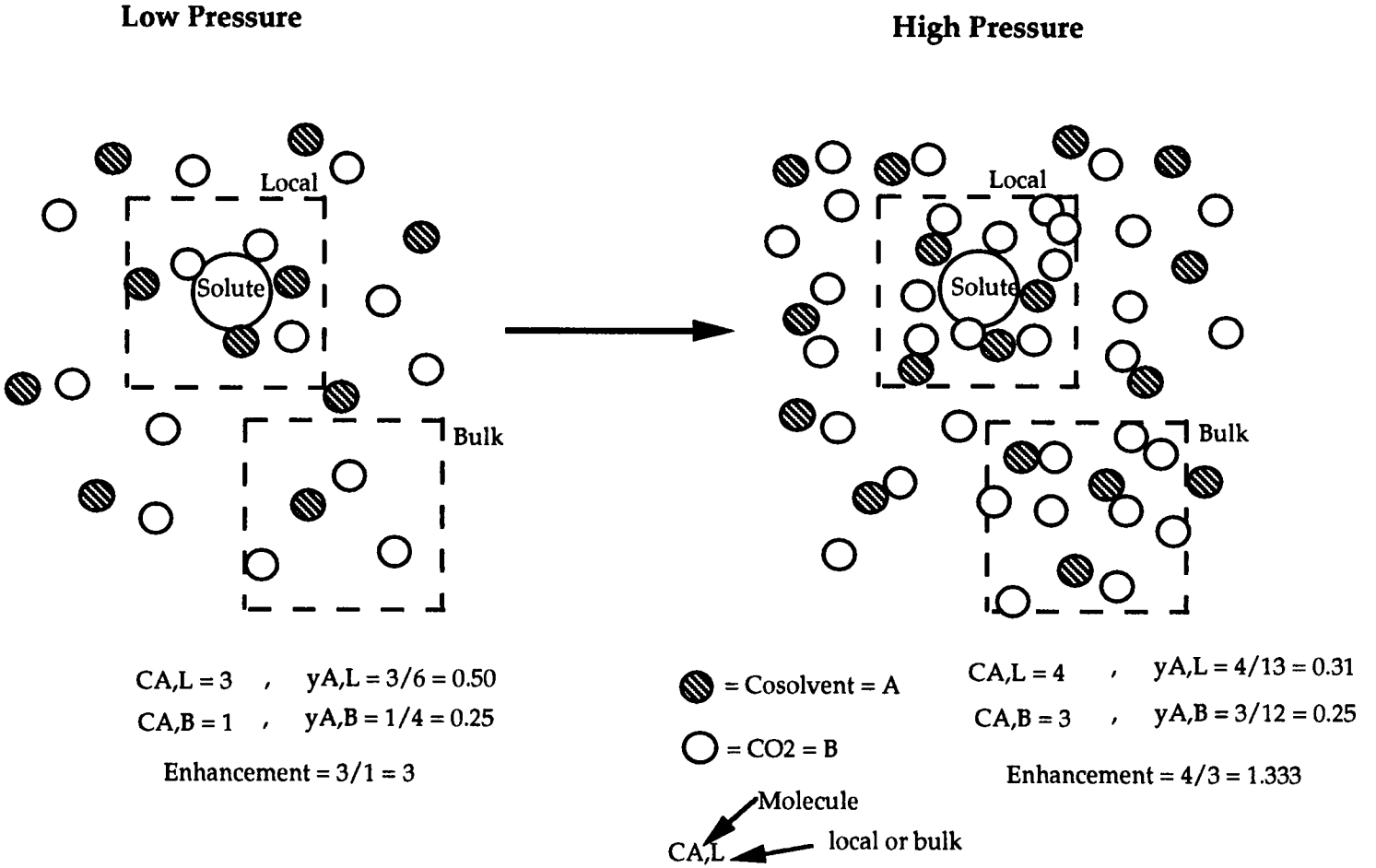


Figure 4-21 Absolute local concentration versus local composition enhancement of cosolvent around solute molecules.

enhancement with increasing system pressure would lead to the observed decrease in cosolvent effect. There are several possible mechanisms that have been used to describe the cosolvent effect. One study (Van Alsten, 1986) was based on measurements of polar and nonpolar solute solubility in pure and modified SC-CO_2 and concluded that the polarity of both solute and cosolvent and also the H-bonding might play important roles to enhance the cosolvent effect. The cosolvents used by Van Alsten were methanol and acetone with polar solutes (acridine and 9-fluorenone) and nonpolar solutes (phenanthrene and fluorene). The dipole moments of these solutes and cosolvents are shown in Table 4-1. For acridine, methanol gave the stronger cosolvent effect than acetone, which indicated that the cosolvent H-bonding has a stronger influence than the polarities of the solute and the cosolvent. Acridine is a strong base (H-bond acceptor) while methanol is a strong H-bond donor, allowing this mechanism. For 9-fluorenone, which has the largest solute dipole moment, acetone was found to be a better cosolvent, which showed cosolvent polarity affects the cosolvent-solute interaction. For polar solutes, the cosolvent effect is a strong function of cosolvent polarity, while in nonpolar systems, such as phenanthrene in modified SC-CO_2, both methanol and acetone showed little effect at low concentrations (1 mol %). However, the cosolvent effect increased significantly as the amount of cosolvent increased above 1 mol % (4 mol % of methanol and 2.5 mol % of acetone). Solubility of nonpolar solutes, such as phenanthrene, in modified SC-CO_2 showed little increase, unlike polar solutes.

Table 4-1 Dipole moment of compounds (Van Alsten, 1986)

Class	Compound	Dipole moment (Debye)
Polar solute	9-fluorenone	3.4
	Acridine	2.1
Nonpolar solute	Fluorene	0
	Phenanthrene	0
Cosolvent	Acetone	2.9
	Methanol	1.7

This means the similarity in polarity of the solute-cosolvent is an important factor.

A similar explanation can be applied to this study, since both methanol and acetone had less effect on the solubility of TCMTB than on tebuconazole when added to SC-CO_2. This might be because TCMTB is a nonpolar solute. For tebuconazole, there are two possible mechanisms. First, the polarity of tebuconazole plays an important role in the cosolvent effect because acetone, which has higher polarity than methanol, gave a higher cosolvent effect than methanol. Second, because tebuconazole contains the -OH group, H-bonding could be important. Therefore tebuconazole can be assumed to be an H-bond

donor whose solubility increases when an H-bond acceptor like acetone is used as a cosolvent. Since methanol is a strong H-bond donor, it would not be a suitable cosolvent for tebuconazole, based on H-bonding effects. If solubility enhancement is due to H-bonding, raising the system temperature should result in a decrease in the observed cosolvent effect. From Figures 4-18 and 4-19, the cosolvent effect of tebuconazole at temperature 65 °C was much less than at 50 °C, which supports the proposed tebuconazole-acetone H-bonding mechanism. The existence of this mechanism would be proven if data for TCMTB and tebuconazole dipole moments and the degree of intermolecular H-bonding between solutes and cosolvents at these conditions were studied using a simple oscillator circuit for capacitance measurements, adapted from Bonilla and Vassos, (1977) to measure dipole moment and FTIR spectroscopy (Fulton, et al., 1991) to measure the degree of intermolecular H-bonding. Thus the dipole moment of the solutes and the degree of intermolecular H-bonding between solute molecules and cosolvent molecule should be studied at experimental condition used in these solubility studies.

As discussed previously, the shape of the plot of cosolvent effect versus pressure can change from monotonically increasing to monotonically decreasing as more cosolvent is used (Schmitt and Reid, 1986 b; Ting et al, 1993). At constant temperature and pressure, increases in the concentration of either cosolvent increased the cosolvent effect for TCMTB and tebuconazole (Figures 4-22 and 4-23). This suggests that higher cosolvent concentrations

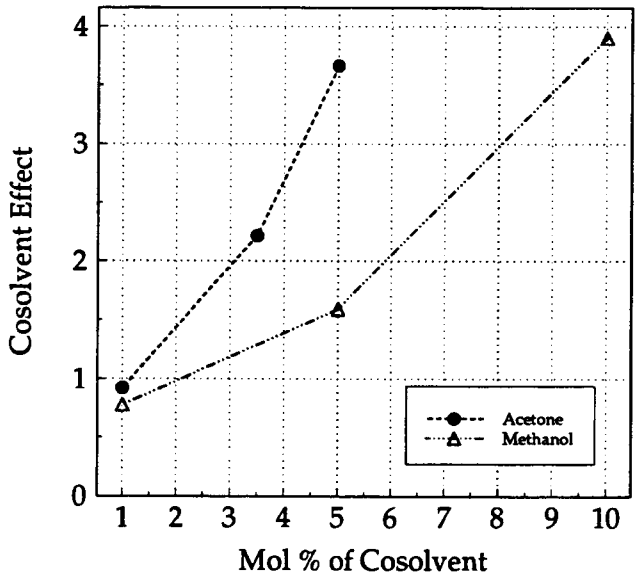


Figure 4-22 Cosolvent effect for TCMTB as a function of cosolvent concentration at 65 °C and 150 bar.

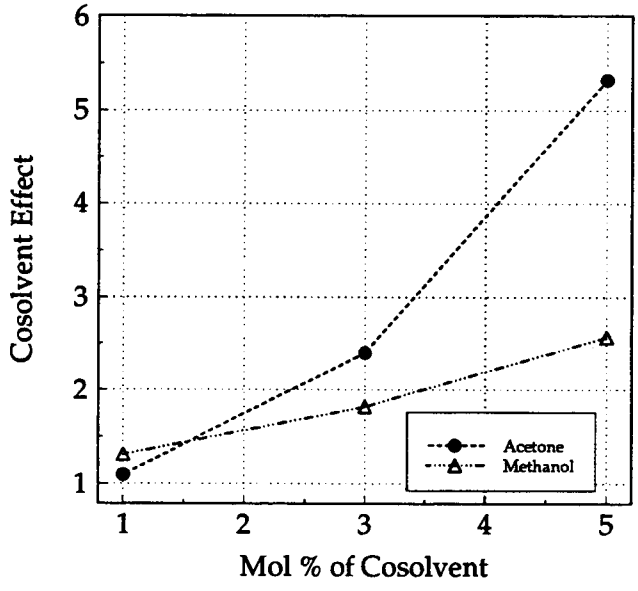


Figure 4-23 Cosolvent effect for tebuconazole as a function of cosolvent concentration at 65 °C and 150 bar.

modify the bulk properties of the fluid to a significant extent (Joshi and Prausnitz, 1984).

4.2 Vapor Pressure Experimental Results

In order to apply the Ziger and Eckert solubility condition, the vapor pressure of the solute must be known. The manufacturers of TCMTB and tebuconazole provided limited data on their vapor pressures. The same apparatus used to determine the solubility of biocides in pure and modified SC-CO_2 was used to measure the vapor pressure of TCMTB at 40 and 70 °C using the gas saturation technique. Instead of CO_2 gas, nitrogen gas was used as a bulk fluid at approximately 1.01 bar. Ten experiments were performed for vapor pressure measurements, five at 40 °C and five at 70 °C. Three of the ten experiments were discarded as outliers, since they were different by one to two orders of magnitude. This data and results provided by Buckman Laboratories (Jonas, 1990) are shown in Table 4-2 and in Figure 4-24. In Figure 4-24, the solid line represented the fitted line to the Buckman data based on the Clausius-Clapeyron equation (Appendix G). It can be seen that data from this study was in good agreement with the fit to Buckman data at 40 °C while at 70 °C there were larger variations. The two most similar data points measured here at each temperature were both below the value predicted by the Buckman data. Assuming the Buckman data is correct, this apparatus can be used to roughly measure the vapor pressure of a pure substance which has

Table 4-2 Vapor pressure data of TCMTB

Source	T(°C)	P(bar)
This thesis	40	1.96×10^{-8}
This thesis	40	1.92×10^{-8}
This thesis	40	3.41×10^{-8}
This thesis	70	1.25×10^{-7}
This thesis	70	1.93×10^{-7}
This thesis	70	1.33×10^{-7}
This thesis	70	5.06×10^{-7}
Buckman	20	3.25×10^{-9}
Buckman	25	5.39×10^{-9}
Buckman	50	5.33×10^{-8}
Buckman	50	7.92×10^{-8}
Buckman	60	1.50×10^{-7}
Buckman	60	2.15×10^{-7}
Buckman	70	2.83×10^{-7}
Buckman	70	4.92×10^{-7}

a vapor pressure as low as 10^{-8} bar at 40 °C to 70 °C only if sufficient replicate experiments are done. This procedure was only used to check the validity of vapor pressure data supplied by Buckman. All calculations in the application of the Ziger and Eckert model used the vapor pressure model based on only Buckman data.

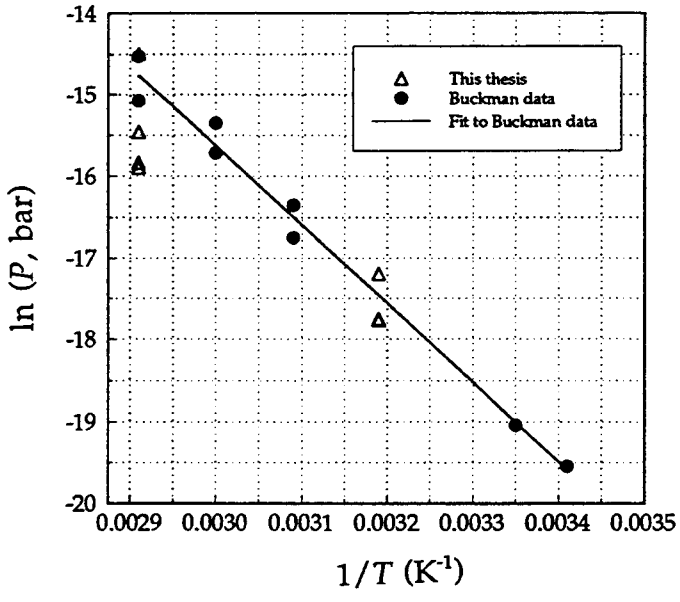


Figure 4-24 Vapor pressure of TCMTB at selected temperatures with a line fitted to the Clausius-Clapeyron equation.

4.3 Data Correlation

4.3.1 Density-based Model

Treatment of the solubility data of biocides in SC-CO_2 using a density-based model resulted in a linear relationship between log w and log ρ as illustrated in Figures 4-3 and 4-4 for TCMTB and tebuconazole, respectively. The linearity provided by this model was excellent, with regression coefficients (R^2) of 0.99 for TCMTB and 0.97 for tebuconazole. The constants γ, β and k from Equation 3.2-16 can be evaluated from the slope of the solubility

isotherms and intercepts on the log w axis at $\rho = 1$. The number of solvent molecules in the solvato complex is represented by the k value listed in Table 4-3.

The effect of temperature on biocide solubility, which depends on the parameter γ, can be related to the melting point of biocide (Maheshwari et al., 1992). As shown in Table 4-3, tebuconazole has a higher melting point than TCMTB and a γ value (-27,940) with a larger absolute value than that of TCMTB (-8,276). Average k values were 6.98 for TCMTB and 6.80 for tebuconazole. It is important to note that k values at different temperatures were the same for TCMTB (k=7.01 at 50 °C and k=6.95 at 65 °C) but slightly different for tebuconazole (k=7.0 at 50 °C and k=6.60 at 65°C). Thus k is temperature dependent in the system of tebuconazole and SC-CO_2, which suggests that the number of solvent molecules involved in the solvato complex decreased with increasing temperature. As clearly shown in Figure 4-4, tebuconazole data did not fit the regression lines as well as TCMTB, so it is not surprising that the two k values are different. This might be because of the polarity of tebuconazole as discussed in Chapter 3 and by Gurdial et al., (1989). Based on the regressions, the relationships between solubility and density would be given by Equations 4-1 and 4-2.

For TCMTB :

$$\log w = 5.98 \log\rho - \frac{1}{2.303}\left(\frac{8276}{T} + 20.28\right) \qquad \textbf{4-1}$$

Table 4-3 Regression parameters from density-based model

Solute	M.P.(°C)	T(°C)	k	R^2	k_{av}	γ	β
TCMTB	35-37	50	7.01	0.99	6.98	-8276	-20.28
	35-37	65	6.95	0.99			
tebuconazole	104-107	50	7.0	0.97	6.80	-27940	40.29
	104-107	65	6.60	0.97			

For tebuconazole :

$$\log w = 5.80 \log \rho - \frac{1}{2.303}\left(\frac{27940}{T} - 40.29\right) \qquad \textbf{4-2}$$

4.3.2 Ziger and Eckert Model

The use of the Ziger and Eckert model requires pure component properties of biocides, such as vapor pressure and P_c. Atomic and group contribution methods were used to estimate P_c (Lyman, 1955) (Appendix E) and δ (Fedors, 1974) (Appendix F) and the Clausius-Clapeyron equation was used to correlate the vapor pressure data of biocides (Appendix G).

The Ziger and Eckert model provided a good correlation of experimental enhancement factors for both biocides. Both TCMTB and tebuconazole showed linear behavior with the solubility isotherms collapsing to a single line as shown in Figures 4-25 and 4-26. The value of the two parameters, η_1 and ϑ_2, can be evaluated from the slope and intercept of each plot and are shown in Table 4-4. In this study, η_1 for both biocides, which is a constant characteristic to each solvent type, were different from the reported value of 0.497 for nonpolar compounds in SC-CO_2 (Yun et al.,1991; Gurdial and Foster, 1991; Gurdial et al., 1989). The deviation may have resulted from the fact that P_c and δ of the biocides were not available and were estimated using the atomic and group contribution methods, which may produce significant errors. For tebuconazole, η_1 is 0.309, slightly greater than 0.28 which was reported for compounds contained one -OH group in their molecular structure (Yun et al., 1991). The difference may have been caused by the presence of the -Cl group in tebuconazole's structure, which increased the value of η_1. A similar explanation can be used for TCMTB, where the presence of the -CNS group decreased the value of η_1 to 0.441 instead of the reported 0.497.

The relationships which was used to predict the solubility of biocides in SC-CO_2 in terms of the enhancement factor (E) and $(\varepsilon^*_A\Delta/y_B(2-\Delta/y_B)-\log(1+\delta_B^2/P))$ can be described by Equations 4-3 and 4-4.

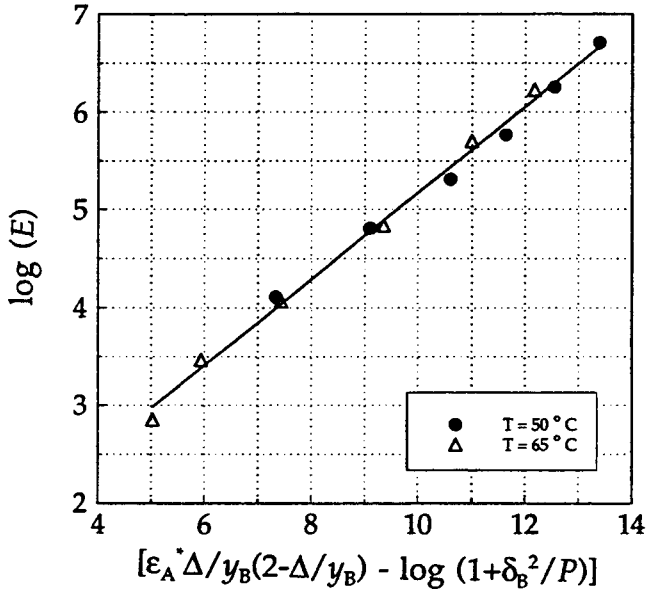


Figure 4-25 Solubility of TCMTB in SC-CO_2 correlated using the Ziger and Eckert model.

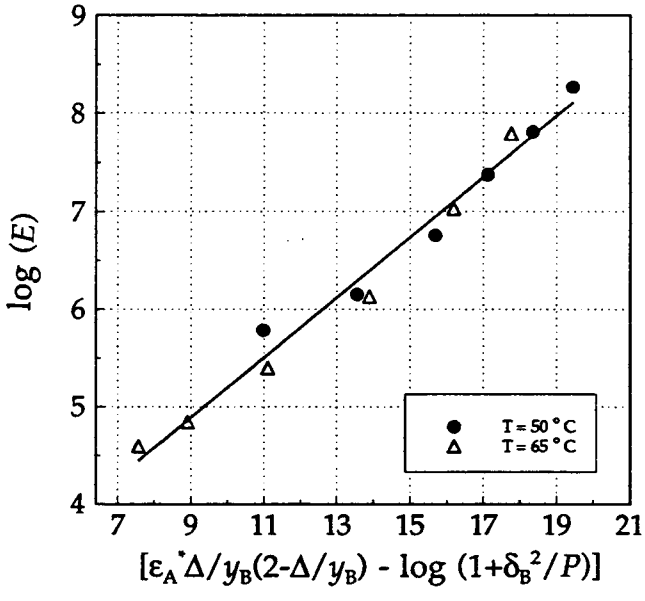


Figure 4-26 Solubility of tebuconazole in SC-CO_2 correlated using the Ziger and Eckert model.

Table 4-4 Regression coefficient and the parameters for the Ziger and Eckert model for solubility in SC-CO_2

Solute	η_1	ϑ_2	R^2
TCMTB	0.441	0.766	0.994
tebuconazole	0.309	2.11	0.980

For TCMTB :

$$\log E = 0.441\left[\varepsilon_A^* \frac{\Delta}{y_B}\left(2 - \frac{\Delta}{y_B}\right) - \log\left(1 + \frac{\delta_B^2}{P}\right)\right] + 0.766 \qquad \textbf{4-3}$$

For tebuconazole :

$$\log E = 0.309\left[\varepsilon_A^* \frac{\Delta}{y_B}\left(2 - \frac{\Delta}{y_B}\right) - \log\left(1 + \frac{\delta_B^2}{P}\right)\right] + 2.11 \qquad \textbf{4-4}$$

The average absolute relative deviations (AARD) in mole fraction as defined in Equation 4-5 are presented in Table 4-5.

$$\text{AARD} = \frac{1}{N}\Sigma\left|\frac{(y_A^{cal} - y_A^{exp})}{y_A^{exp}}\right| \qquad \textbf{4-5}$$

The density-based model seems to give a better fit than the Ziger and Eckert model, since a lower % AARD was observed at 50 and 65 °C. Density-based model is a simple model and gives a relatively easy way to describe the

Table 4-5 Percentage deviation between correlation and experimental solubility in SC-CO_2

Model	Solute	T(°C)	% AARD
Density-based	TCMTB	50	8.55
		65	13.21
	tebuconazole	50	27.41
		65	34.56
Ziger and Eckert	TCMTB	50	19.65
		65	18.59
	tebuconazole	50	30.91
		65	35.48

effect of temperature and pressure on biocide solubility. Although the % AARD of the Ziger and Eckert model is slightly higher than that of density-based model, it still gives better insight on the rate of solute enhancement change with the solvent strength, and provided the advantage of using temperature independent constants, η_1 and ϑ_2, which can reduce the number of the experiments required.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

A continuous flow apparatus was used to determine the solubility of TCMTB and tebuconazole in pure and modified SC-CO_2. The solubility experimental conditions ranged from 100 bar to 300 bar and from 50 to 65 °C. The effect of pressure on TCMTB and tebuconazole solubility in SC-CO_2 followed the expected trend of increasing solubility with an isothermal increase in pressure. The crossover pressures for TCMTB and tebuconazole were located at 196 and 182 bar, respectively. The volatility of the solute and the size of the solute molecule seem to indicate the solubility of biocides in SC-CO_2, i.e. the solute with higher vapor pressure and smaller size showed higher solubility in SC-CO_2.

The introduction of a cosolvent was shown to significantly increase solubility for tebuconazole but had less effect on TCMTB solubility. There are several mechanisms that influence the behavior of the cosolvent effect for these biocides in modified SC-CO_2 : competing effects due to local composition enhancement or the absolute local concentration, the polarity of the solute and the cosolvent, and specific interactions such as H-bonding between solute and cosolvent. However, the mechanism to explain the cosolvent effect behavior remains unclear. Further experiments are needed and are outlined in the

following section. The amount of cosolvent used seemed to be more important than the choice of solvent used.

Ten gas saturation experiments were conducted to measure the vapor pressure of TCMTB using the same apparatus used for solubility studies. The vapor pressure experimental conditions were at approximately 1.01 bar and either 40 or 70 °C. It was found that 7 out of 10 experimental data were in the same range (~10^{-8} bar) as vapor pressure data provided by Buckman Laboratories, Inc.. Therefore, this apparatus under carefully controlled conditions could be used to estimate the vapor pressure of compounds down to approximately 10^{-8} bar.

All experimental solubility data of TCMTB and tebuconazole in SC-CO_2 were correlated using both a density-based model and the Ziger and Eckert model. The density-based model provided a good correlation of the experimental results and the maximum % AARD for mole fraction was 13.21 and 34.56 for TCMTB and tebuconazole, respectively. The parallel straight lines obtained for TCMTB, indicated that the average number of solvent molecules involved in the postulated solvato complex was temperature independent. On the other hand, the more polar tebuconazole appear to have fewer solvent molecules in the solvato complex at the higher temperature (65 °C *vs* 50 °C).

The Ziger and Eckert model also gave a good correlation of experimental enhancement factors for both biocides and showed linear

behavior with the solubility isotherms collapsing to a single line. The maximum % AARD for mole fraction was 19.65 for TCMTB and 35.48 for tebuconazole. Density-based model is a simple model and gives a relatively easy way to describe the effect of temperature and pressure on the solubility of biocides. Even though the %AARD using the Ziger and Eckert model was higher than that obtained for density-based model, the Ziger and Eckert model provided an excellent prediction of solubility and had the advantage of using temperature independent constants, η_1 and ϑ_2, thus reducing the number of experiments required.

5.2 Recommendations for Future Work

(1) Although the effects of pressure, temperature and cosolvent on the solubility of two biocides have been studied, more work is required for a better understanding and utilization of the system. The polarity of the solutes and cosolvent is one of the important factors used to explain the behavior of cosolvent effect in ternary systems. To determine the importance of cosolvent polarity on the solubility of TCMTB and tebuconazole, a series of cosolvents with significantly different dipole moments should be used. If polarity is a significant effect, the solubility increase should correlate with increase in cosolvent dipole moment.

(2) The H-bonding and local concentration of cosolvent around the solute are also important effects to be studied. The FTIR spectroscopy can be

used to study the degree of H-bonding in SCF at particular conditions and fluorescence spectroscopy and molecular dynamics simulation could be used to estimate the local concentration of cosolvent around a solute molecule.

(3) In order to correlate and model the solvent-solute system, the physical properties of the solute must be known, such as the dipole moment, T_c, P_c and vapor pressure. These may be obtained from experimental studies or estimated using empirical methods such as atomic and group contribution methods.

(4) Unlike a solid, where the solubility of the SCF solvent in the dense phase was assumed negligible, for liquid\SCF systems the compositions of both phases change with mixing and the solute phase is not a pure compound. To study and model solubility of biocides which are liquid at supercritical conditions for the solvent, the current experimental apparatus would need to be modified to allow sampling of both phases.

(5) The melting points of some solids have been observed to decrease when certain cosolvents or mixed solutes are used with them (Brennecke and Eckert, 1989 ; Dobbs, 1987). This might be a result of a small amount of the cosolvent or the second solute dissolving in them to form a liquid phase. Such complicated phase behavior must be studied in more sophisticated apparatus, such as a variable volume view cell system.

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Appendices

Appendix A : Pressure Drop Across the View Cell

Pressure (bar)	Pressure drop (bar)	% Deviation
100	4.07	4.07
200	3.59	1.79
300	2.14	0.71

Appendix B : Conditions for HPLC

Solute	:	TCMTB
Wave length	:	280 nm
Mobile phase A	:	Acetonitrile 55% v/v / Buffer 45% v/v
Mobile phase B	:	Acetonitrile 95% v/v / Buffer 05% v/v
Buffer Solution	:	0.5% weight by volume of $NH_4(CO_3)_2$ in deionized water 562
Flow rate	:	1.5 cm^3/min, time file 2
Injection	:	10 µl loop

Appendix C : HPLC Calibration for TCMTB

Concentration (μg/ml)	Peak height × 10^{-4}
0	0
20	26.48675
40	52.20840
100	130.22970
300	383.74805
500	626.27035

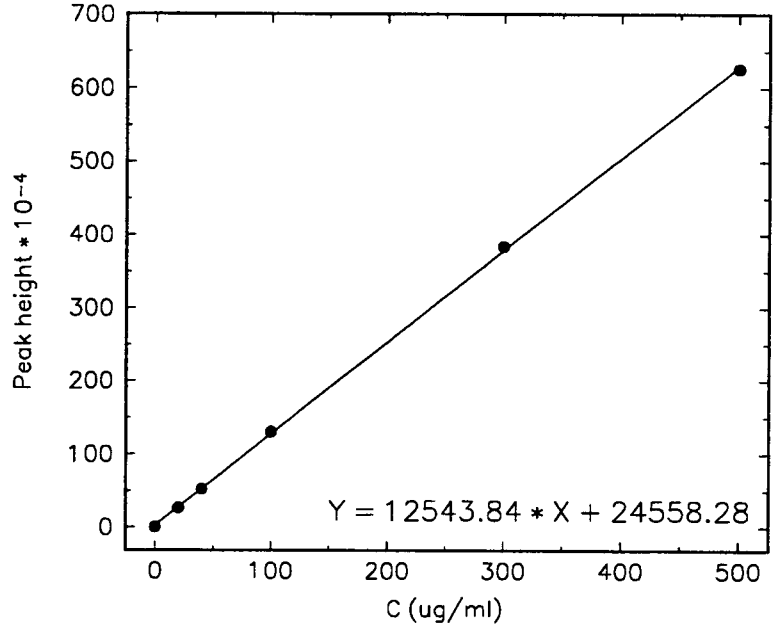


Figure C-1 HPLC calibration of TCMTB in the range of 0 - 500 μg/ml (See conditions in Appendix B).

Appendix D : Solubility Data

Table D-1 Solubility of TCMTB in SC-CO_2 at (A) 50 ° C and (B) 65 °C

(A)

P (bar)	Weight Fraction($\times 10^4$)	Mole Fraction($\times 10^5$)	Standard* Deviation($\times 10^4$)	%Deviation
100	0.466	0.860		
	0.453	0.836		
avg	0.460	0.848	0.009	2.0
110	2.032	3.752		
	2.161	3.990		
	2.002	3.696		
avg	2.065	3.813	0.084	4.09
125	5.964	11.015		
	5.605	10.352		
	5.843	10.790		
avg	5.804	10.719	0.183	3.15
150	14.271	26.375		
	12.999	24.021		
	13.268	24.519		
	13.872	25.636		
	14.919	27.573		
avg	13.866	25.625	0.772	5.57
200	31.943	59.118		
	31.759	58.778		
	31.968	59.166		
avg	31.890	59.021	0.114	0.36
300	59.125	109.671		
	60.482	112.201		
	60.719	112.642		
avg	60.109	111.504	0.860	1.43

* Based on weight fraction calculation. avg = average

Table D-1, Continued.

(B)

P (bar)	Weight Fraction($\times 10^4$)	Mole Fraction($\times 10^5$)	Standard* Deviation($\times 10^4$)	%Deviation
100	0.0942	0.174	-	-
110	0.382	0.705		
	0.324	0.599		
avg	0.353	0.652	0.041	11.62
125	1.278	2.360		
	1.213	2.239		
avg	1.246	2.299	0.046	3.69
150	6.143	11.338		
	5.947	10.978		
	6.024	11.120		
avg	6.038	11.145	0.099	1.64
200	32.109	59.238		
	34.920	64.419		
	33.987	62.700		
avg	33.672	62.119	1.432	4.25
300	79.103	146.968		
	74.399	132.286		
avg	76.751	139.627	3.326	4.33

* Based on weight fraction calculation.
avg = average

Table D-2 Solubility of TCMTB in SC-CO_2 with 3 mol % methanol at (A) 50 ° C and (B) 65 ° C

(A)

P (bar)	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	%Deviation	Cosolvent Effect**
100	0.376			
	0.307			
avg	0.342	0.049	14.21	0.743
125	5.078			
	5.345			
avg	5.211	0.189	3.63	0.898
150	13.716			
	14.094			
avg	13.905	0.267	1.92	1.003
200	37.224			
	37.555			
	38.552			
avg	37.777	0.691	1.83	1.185
300	68.583			
	71.188			
	68.951			
avg	69.574	1.41	2.03	1.157

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-2, Continued.

(B)

P (bar)	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	%Deviation	Cosolvent Effect
125	0.836			
	0.772			
avg	0.804	0.045	5.63	0.645
150	5.285			
	4.804			
	4.550			
avg	4.880	0.373	7.65	0.808
200	33.862			
	30.747			
avg	32.304	2.203	6.82	0.959
300	72.647			
	69.159			
	73.332			
avg	71.712	2.238	3.12	0.934

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-3 Solubility of TCMTB in SC-CO_2 with 1.68 mol % acetone at (A) 50 °C and (B) 65 ° C

(A)

P (bar)	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	% Deviation	Cosolvent Effect
100	0.302			
	0.251			
	0.233			
avg	0.262	0.035	13.54	0.570
150	14.320			
	13.154			
avg	13.737	0.824	6.00	0.991
200	48.749			
	48.108			
	45.560			
avg	47.472	1.687	3.55	1.489
300	85.022			
	89.186			
	89.247			
avg	87.818	2.422	2.76	1.461

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-3, Continued.

(B)

P (bar)	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	% Deviation	Cosolvent Effect
100	0.026			
	0.036			
avg	0.031	0.0072	23.23	0.330
125	0.471			
	0.453			
	0.529			
avg	0.484	0.040	8.26	0.388
200	24.289			
	23.800			
	24.688			
	23.955			
	24.092			
	24.008			
avg	24.139	.314	1.30	0.717
300	60.488			
	66.886			
	60.126			
avg	62.500	3.803	6.08	0.814

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-4 Solubility of TCMTB in SC-CO_2 at 65 °C and 150 bar with (A) methanol (B) acetone

(A)

Mol %	Weight Fraction($\times 10^4$)	Standard* Diviation($\times 10^4$)	% Deviation	Cosolvent Effect
1.0	4.008			
	4.691			
	5.263			
avg	4.654	0.628	13.50	0.777
5.0	9.172			
	10.039			
avg	9.606	0.613	6.38	1.591
10.0	22.386			
	24.648			
	23.655			
avg	23.563	1.134	4.81	3.902

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-4, Continued.

(B)

Mol %	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	% Deviation	Cosolvent Effect
1.0	4.948			
	6.043			
	5.680			
avg	5.557	0.558	10.04	0.920
3.5	12.701			
	14.043			
avg	13.372	0.949	7.10	2.215
5.0	26.308			
	20.905			
	22.117			
avg	23.110	2.835	12.27	3.663

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-5 Solubility of (80.0% pure) TCMTB in SC-CO_2 at 50 °C

P (bar)	Weight @ Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	%Deviation
110	0.320		
	1.275		
	.452		
avg	.682	0.517	75.84
125	1.179		
	4.768		
	5.475		
avg	3.807	2.303	60.50
150	16.157		
	20.784		
	19.302		
avg	18.748	2.363	12.60
200	61.450		
	40.772		
	46.969		
avg	49.730	10.612	21.34
250	60.466		
	72.925		
	61.127		
avg	64.839	7.010	10.81
300	95.583		
	90.600		
	70.004		
avg	85.396	13.56	15.88

* Based on weight fraction calculation. avg = average
@ Ice bath was used as a cold trap.

Table D-6 Solubility of tebuconazole in SC-CO_2 at (A) 50 °C and (B) 65 °C (A)

P (bar)	Weight Fraction($\times 10^4$)	Mole Fraction($\times 10^5$)	Standard* Deviation($\times 10^4$)	%Deviation
100	0.404	0.578		
	0.477	0.682		
avg	0.441	0.630	0.051	11.58
110	0.898	1.283		
	1.049	1.500		
	0.867	1.240		
avg	0.938	1.341	0.097	10.34
125	3.424	4.896		
	3.167	4.529		
	3.432	4.909		
avg	3.341	4.778	0.151	4.52
150	11.538	16.512		
	11.055	15.821		
	11.791	16.874		
	11.386	16.295		
	11.921	17.062		
avg	11.538	16.513	0.342	2.96
200	22.507●	32.241		
	24.058●	34.467		
	28.056■	40.208		
	23.263■	33.325		
	21.502■	30.798		
	20.779O	31.033		
	22.330O	31.987		
avg	23.214	33.437	2.391	10.30
300	43.962	63.091		
	44.158	63.372		
	47.583	68.309		
	43.173	61.954		
avg	44.719	64.181	1.956	4.37

* Based on weight fraction calculation. avg = average

● at CO_2 gas flow rate = 0.1 lit/min., ■ at 0.2 lit/min., O at 0.3 lit/min.

Table D-6, Continued.

(B)

P (bar)	Weight Fraction($\times 10^4$)	Mole Fraction($\times 10^5$)	Standard* Deviation($\times 10^4$)	%Deviation
100	0.230	0.328		
	0.220	0.315		
	0.292	0.417		
avg	0.247	0.354	0.039	15.78
110	0.423	0.604		
	0.381	0.545		
	0.394	0.563		
avg	0.399	0.571	0.022	5.51
125	1.414	2.021		
	1.114	1.593		
avg	1.264	1.807	0.212	16.77
150	5.716	8.177		
	5.247	7.505		
	5.991	8.570		
avg	5.651	8.084	0.376	6.65
200	31.030	44.482		
	30.566	43.815		
	39.634	56.858		
avg	33.743	48.385	5.107	15.13
300	139.515	201.879		
	126.396	182.687		
	125.579	181.495		
	122.345	176.771		
avg	129.147	185.708	7.576	5.87

* Based on weight fraction calculation. avg = average

Table D-7 Solubility of tebuconazole in SC-CO_2 with 3 mol % methanol at (A) 50 °C and (B) 65 °C

(A)

P (bar)	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	%Deviation	Cosolvent Effect**
100	0.513			
	0.461			
	0.532			
avg	0.502	0.037	7.32	1.140
110	2.192			
	2.260			
avg	2.226	0.048	2.16	2.373
125	10.974			
	11.710			
	10.617			
avg	11.100	0.557	5.02	3.322
150	39.632			
	40.607			
avg	40.120	0.689	1.72	3.477
200	81.091			
	80.644			
avg	80.868	0.316	0.39	3.484
300	201.014			
	206.653			
	208.328			
avg	205.332	3.832	1.87	4.592

* Based on weight fraction calculation. avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-7, Continued.

(B)

P (bar)	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	%Deviation	Cosolvent Effect**
100	0.265			
	0.243			
	0.229			
avg	0.246	0.018	7.39	0.996
110	0.509			
	0.521			
	0.498			
avg	0.509	0.012	2.25	1.292
125	1.724			
	1.874			
	1.528			
avg	1.709	0.174	10.15	1.352
150	9.941			
	10.131			
	10.772			
avg	10.281	0.435	4.24	1.819
200	64.941			
	65.881			
	65.954			
avg	65.592	0.565	0.86	1.944
300	260.538			
	257.305			
	259.441			
avg	259.095	1.644	0.63	2.006

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-8 Solubility of tebuconazole in SC-CO_2 with 3 mol % acetone at (A) 50 °C and (B) 65 °C

(A)

P (bar)	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	%Deviation	Cosolvent Effect**
100	1.386			
	1.324			
avg	1.355	0.044	3.23	3.077
110	6.571			
	6.689			
	6.854			
avg	6.705	0.142	2.12	7.148
125	12.817			
	12.041			
	12.604			
avg	12.487	0.401	3.21	3.738
150	31.459			
	31.192			
	31.348			
avg	31.333	0.134	0.43	2.716
200	61.652			
	60.236			
	63.821			
avg	61.903	1.806	2.92	2.667
300	117.994			
	119.955			
	116.678			
avg	118.209	1.649	1.39	2.643

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-8, Continued.

(B)

P (bar)	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	%Deviation	Cosolvent Effect**
100	0.593			
	0.623			
	0.603			
avg	0.606	0.015	2.52	2.453
110	1.208			
	1.153			
avg	1.181	0.039	3.30	2.997
125	3.213			
	3.171			
avg	3.192	0.030	0.93	2.525
150	13.816			
	13.354			
	13.500			
avg	13.557	0.263	1.94	2.399
200	63.694			
	63.611			
avg	63.653	0.059	0.09	1.886
300	173.692			
	172.592			
	173.119			
avg	173.134	0.550	0.32	1.341

* Based on weight fraction calculation. avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-9 Solubility of tebuconazole in SC-CO_2 at 65 °C and 150 bar with (A) methanol (B) acetone

(A)

Mol %	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	% Deviation	Cosolvent Effect
1.0	7.408			
	7.235			
	7.580			
avg	7.408	0.173	2.33	1.311
3.0	9.941			
	10.131			
avg	10.772			
	10.281	0.435	4.24	1.819
5.0	14.612			
	14.411			
	14.523			
avg	14.515	0.101	0.69	2.569

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-9, Continued.

(B)

Mol %	Weight Fraction($\times 10^4$)	Standard* Deviation($\times 10^4$)	% Deviation	Cosolvent Effect
1.0	6.155			
	6.218			
	6.143			
avg	6.172	0.040	0.65	1.092
3.0	13.816			
	13.354			
	13.500			
avg	13.557	0.263	1.94	2.399
5.0	29.825			
	29.986			
	30.453			
avg	30.088	0.326	1.08	5.324

* Based on weight fraction calculation.
avg = average

** Cosolvent Effect is defined as the ratio of the solubility of solute in cosolvent-SC-CO_2 to the solubility of solute in SC-CO_2.
Cosolvent Effect(CE) = y^{ter}/y^{bi}

Table D-10 Solubility of phenol in SC-CO_2 at 60 °C

P (bar)	Mole Fraction($\times 10^2$)	Standard* Deviation($\times 10^2$)	%Deviation
170	2.286		
	2.307		
	2.272		
avg	2.288	0.018	0.08
200	2.832		
	2.962		
	3.097		
avg	2.964	0.133	4.47
230	4.204		
	4.285		
avg	4.245	0.057	1.35

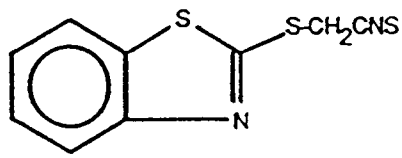
* Based on weight fraction calculation.
avg = average

Table D-11 Density of CO_2

P (bar)	ρ at 50 °C (kg/m^3)	ρ at 65 °C (kg/m^3)
100	387.69	265.66
110	504.91	320.62
125	616.60	416.95
150	702.98	556.84
200	785.77	694.51
250	835.41	763.37
300	871.52	809.70

Appendix E : Critical Properties Estimation

TCMTB *(2-(Thiocyanomethylthio) benzothiazole)*



Vetere's Correlation(Vetere, 1973)

Critical Volume

$$V_c = 33.04 + (\Sigma M_i \Delta v_i)^{1.029}$$

M_i is Molecular weight of group i

Group	number of group	Δv_i	M_i
Ring Increment			
(-CH=)	4	2.538	13.019
(-C=)	3	2.538	12.011
(-S-)	1	0.911	32.066
(-N=), (-N-)	1	1.883	14.007
Nonring Increment			
(-CH2-)	1	3.360	14.027
(-S-)	1	0.591	32.066
(-N=), (-N-)	1	1.793	14.007
(=S)	1	0.591	32.006
(=C=)	1	2.908	12.011

$$\Sigma M_i \Delta v_i = 4(13.019)(2.538) + 3(12.011)(2.538) + 1(32.066)(0.911) +$$
$$1(14.007)(1.883) + 1(14.027)(3.360) + 1(32.066)(0.591) +$$
$$1(14.007)(1.793) + 1(32.066)(0.591) + 1(12.011)(2.908)$$

$$\Sigma M_i \Delta v_i = 424.283$$

$$V_c = 33.04 + (424.283)^{1.029}$$

$$V_c = 538.70 \qquad \left[\frac{cm^3}{mol}\right]$$

Lyderson's Correlation (Lyderson, 1955)

Critical Pressure

$$P_c = \frac{M}{(0.34 + \Sigma \Delta P)^2}$$

M is the molecular weight of TCMTB = 238.36

Critical Temperature

$$\frac{T_c}{T_b} = \frac{1}{0.567 + \Sigma \Delta T - (\Sigma \Delta T)^2}$$

T_b is the normal boiling point of TCMTB, which is not known and must be estimated (Miller, 1977).

Group	number of group	ΔT	ΔP
Ring Increment			
(-CH=)	4	0.011	0.154
(-C=)	3	0.011	0.154
(-S-)	1	0.008	0.240
(-N=), (-N-)	1	0.007	0.130
Nonring Increment			
(-CH2-)	1	0.020	0.227
(-S-)	1	0.015	0.270
(-N=), (-N-)	1	0.014	0.170
(=S)	1	0.003	0.240
(=C=)	1	0.0	0.198

$$\Sigma\Delta P = 4(0.154) + 3(0.154) + 1(0.240) + 1(0.130) + 1(0.270) + 1(0.227) + 1(0.170) + 1(0.240) + 1(0.198)$$

$$\Sigma\Delta P = 2.553$$

$$P_c = \frac{238.36}{(0.34 + 2.553)^2}$$

$$P_c = 28.48 \quad \text{atm}$$

$$\Sigma\Delta T = 4(0.011) + 3(0.011) + 1(0.008) + 1(0.007) + 1(0.015) + 1(0.020) + 1(0.014) + 1(0.003) + 1(0.0)$$

$$\Sigma\Delta T = 0.144$$

$$\frac{T_c}{T_b} = \frac{1}{0.567 + 0.144 - (0.144)^2}$$

$$\frac{T_c}{T_b} = 1.449$$

Normal boiling Temperature

$$T_b = 0.012186\,\theta\, e^{\beta}$$

$$\theta = \frac{T_b}{T_c} = \frac{1}{1.449} = 0.690$$

$$\beta = \frac{[(1-\theta)^{\frac{2}{7}} - 0.048]\ln(V_c) + (1-\theta)^{\frac{2}{7}}\ln(P_c) + 1.255}{(1-\theta)^{\frac{2}{7}}}$$

$$\beta = \frac{[(1-0.69)^{\frac{2}{7}} - 0.048]\ln(538.70) + (1-0.69)^{\frac{2}{7}}\ln(28.48) + 1.255}{(1-0.69)^{\frac{2}{7}}}$$

$$\beta = 10.970$$

$$T_b = 0.012186(0.69)e^{10.970}$$

$$T_b = 488.563 \quad K$$

$$T_c = 707.928 \quad K$$

Critical properties of TCMTB

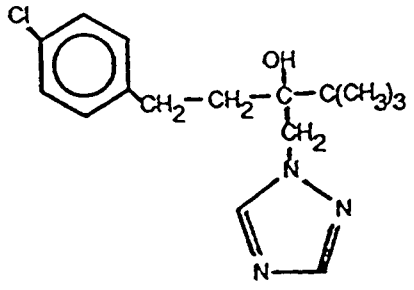
T_c = 707.928 K

P_c = 28.48 atm = 28.86 bar

V_c = 538.70 cm^3/mol

Normal boiling temperature (T_b) = 488.563 K

Tebuconazole (*α-[2-(4-chlorophenyl) ethyl]-α-(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol*)



Vetere's Correlation(Vetere, 1973)

Critical Volume

$$V_c = 33.04 + (\Sigma M_i \Delta v_i)^{1.029}$$

M_i is Molecular weight of group i

Group	number of group	Δv_i	M_i
Ring Increment			
(-CH=)	6	2.538	13.019
(-C=)	2	2.538	12.011
(-Cl)	1	1.237	35.453
(-N=), (-N-)	3	1.883	14.007
Nonring Increment			
(-CH3)	3	3.360	15.035
(-CH2-)	3	3.360	14.027
(-C-)	2	3.360	12.011
(-OH)	1	0.704	16.126

$$\Sigma M_i \Delta v_i = 6(13.019)(2.538) + 2(12.011)(2.538) + 1(35.453)(1.237) +$$
$$3(14.007)(1.883) + 3(15.035)(3.360) + 3(14.027)(3.360) +$$
$$2(12.011)(3.360) + 1(16.126)(0.704)$$

$$\Sigma M_i \Delta v_i = 767.214$$

$$V_c = 33.04 + (424.283)^{1.029}$$

$$V_c = 963.246 \qquad \left[\frac{cm^3}{mol}\right]$$

Lyderson's Correlation (Lyderson, 1955)

Critical Pressure

$$P_c = \frac{M}{(0.34 + \Sigma \Delta P)^2}$$

M is the molecular weight of tebuconazole = 307.83

Critical Temperature

$$\frac{T_c}{T_b} = \frac{1}{0.567 + \Sigma \Delta T - (\Sigma \Delta T)^2}$$

T_b is the normal boiling point of tebuconazole, which is not known and must be estimated (Miller, 1977).

Group	number of group	ΔT	ΔP
Ring Increment			
(-CH=)	6	0.011	0.154
(-C=)	2	0.011	0.154
(-Cl)	1	0.017	0.320
(-N=), (-N-)	3	0.007	0.130
Nonring Increment			
(-CH3)	3	0.020	0.227
(-CH2-)	3	0.020	0.227
(-C-)	2	0.000	0.210
(-OH)	1	0.082	0.060

$$\Sigma\Delta P = 6(0.154) + 2(0.154) + 1(0.320) + 3(0.130) + 3(0.227) + 3(0.227) + 2(0.210) + 1(0.060)$$

$$\Sigma\Delta P = 3.784$$

$$P_c = \frac{307.83}{(0.34 + 3.784)^2}$$

$$P_c = 18.10 \quad \text{atm}$$

$$\Sigma\Delta T = 6(0.011) + 2(0.011) + 1(0.017) + 3(0.007) + 3(0.020) + 3(0.020) + 2(0.000) + 1(0.082)$$

$$\Sigma\Delta T = 0.328$$

$$\frac{T_c}{T_b} = \frac{1}{0.567 + 0.328 - (0.328)^2}$$

$$\frac{T_c}{T_b} = 1.270$$

Normal boiling Temperature

$$\theta = \frac{T_b}{T_c} = \frac{1}{1.270} = 0.787$$

$$T_b = 0.012186\,\theta\, e^{\beta}$$

$$\beta = \frac{[(1-\theta)^{\frac{2}{7}} - 0.048]\ln(V_c) + (1-\theta)^{\frac{2}{7}}\ln(P_c) + 1.255}{(1-\theta)^{\frac{2}{7}}}$$

$$\beta = \frac{[(1-0.787)^{\frac{2}{7}} - 0.048]\ln(963.246) + (1-0.787)^{\frac{2}{7}}\ln(18.10) + 1.255}{(1-0.787)^{\frac{2}{7}}}$$

$$\beta = 11.205$$

$$T_b = 0.012186(0.787)e^{11.205}$$

$$T_c = 895.608 \quad K$$

$$T_b = 705.203 \quad K$$

Critical properties of tebuconazole

T_c = 895.608 K

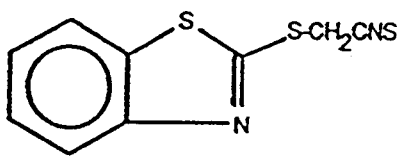
P_c = 18.10 atm = 18.34 bar

V_c = 963.246 cm^3/mol

Normal boiling temperature (T_b) = 705.203 K

Appendix F : Solubility Parameter Estimation (Fedors, 1974)

TCMTB *(2-(Thiocyanomethylthio) benzothiazole)*



Group	number of group	Δe_i(cal/mol)	Δv_i(cm^3/mol)
(-CH2-)	1	1180	16.1
(-CH=)	4	1030	13.5
(-C=)	3	1030	-5.5
(-S-)	2	3380	12.0
(-N=)	1	2800	5.0
(-CNS)	1	4800	37.0
(Ring closure 5 or more atom)	2	250	16.0
(Conjugation in ring for each double bond)	3	400	-2.2

$\Sigma\Delta e_i$ = 1(1180) + 4(1030) + 3(1030) + 2(3380) + 1(2800) + 1(4800) + 2(250) + 3(400)

$\Sigma\Delta e_i$ = 24450 cal/mol

$\Sigma\Delta v_i$ = 1(16.1) + 4(13.5) + 3(-5.5) + 2(12.0) + 1(5.0) + 1(37.0) + 2(16) + 3(-2.2)

$\Sigma\Delta v_i$ = 145 cm^3/mol

$$\delta = \left[\frac{\sum_i \Delta e_i}{\sum_i \Delta v_i}\right]^{\frac{1}{2}}$$

$$\delta = \left[\frac{24450}{145}\right]^{\frac{1}{2}}$$

$\delta_{TCMTB} = 12.99$ $(cal/cm^3)^{1/2}$ at 25 ° C

$\delta_{T_2} = \delta_{T_1}(1+1.13\alpha(T_1-T_2))$

$\alpha = 0.0007\ K^{-1}$ based on naphthalene data

$\delta_{50} = 12.99(1+1.13(0.0007)(298.15-323.15))$

$\delta_{50} = 12.73$ $(cal/cm^3)^{1/2}$ at 50 ° C

$\delta_{65} = 12.99(1+1.13(0.0007)(298.15-338.15))$

$\delta_{65} = 12.58$ $(cal/cm^3)^{1/2}$ at 65 ° C

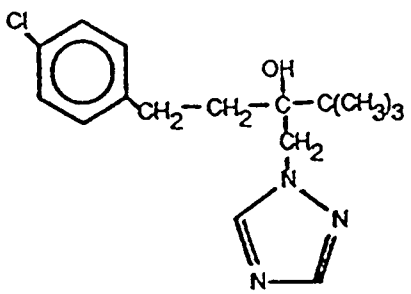
$V_{25} = 145.0$ (cm^3/mol) at 25°C

$V_{T_2} = V_{T_1}[1+\alpha(T_2-T_1)]$

$V_{50} = 147.54$ (cm^3/mol) at 50°C

$V_{65} = 149.06$ (cm^3/mol) at 65°C

Tebuconazole (α-*[2-(4-chlorophenyl) ethyl]*-α-*(1,1-dimethylethyl)-1H-1,2,4-triazole-1-ethanol*)



Group	number of group	Δe_i(cal/mol)	Δv_i(cm^3/mol)
(CH3)	3	1125	33.5
(-CH2-)	3	1180	16.1
(-CH=)	6	1030	13.5
(-C=)	2	1030	-5.5
(C)	2	350	-19.2
(Cl)	1	2760	24.0
(-N=)	2	2800	5.0
(-N-)	1	1000	-9.0
(-OH)	1	7120	10.0
(Ring closer 5 or more atom)	2	250	16.0
(Conjugation in ring for each double bond)	3	400	-2.2
(Halogen attach to carbon atom with double bond)	1	552	4.0

$\Sigma\Delta e_i$ = 3(1125) + 3(1180) + 6(1030) + 2(1030) + 2(350) + 1(2760) + 2(2800) + 1(1000) + 1(7120) + 3(400) + 2(250) - 1(552)

$\Sigma\Delta e_i$ = 33483 cal/mol

$\Sigma\Delta v_i$ = 3(33.5) + 3(16.1) + 6(13.5) - 2(5.5) - 2(19.2) + 1(24.0) + 2(5.0) - 1(9.0) + 1(10.0) - 3(2.2) + 2(16) + 1(4.0)

$\Sigma\Delta v_i$ = 244.8 cm^3/mol

$$\delta = \left[\frac{\sum_i \Delta e_i}{\sum_i \Delta v_i}\right]^{\frac{1}{2}}$$

$$\delta = \left[\frac{33483}{244.8}\right]^{\frac{1}{2}}$$

$\delta_{tebuconazole} = 11.70$ $(cal/cm^3)^{1/2}$ at 25°C

$$\delta_{T_2} = \delta_{T_1}(1+1.13\alpha(T_1-T_2))$$

$\alpha = 0.0007\ K^{-1}$ based on naphthalene data

$\delta_{50} = 11.70(1+1.13(0.0007)(298.15-323.15))$

$\delta_{50} = 11.46$ $(cal/cm^3)^{1/2}$ at 50°C

$\delta_{65} = 11.70(1+1.13(0.0007)(298.15-338.15))$

$\delta_{65} = 11.33$ $(cal/cm^3)^{1/2}$ at 65°C

$V_{25} = 244.8$ (cm^3/mol) at 25°C

$$V_{T_2} = V_{T_1}[1+\alpha(T_2-T_1)]$$

V_{50} = 249.08 (cm^3/mol) at 50°C

V_{65} = 251.65 (cm^3/mol) at 65°C

Appendix G : Vapor Pressure of Biocides

The vapor pressure of a biocide is a physical property used to calculate the enhancement factor in the Ziger and Eckert model. Vapor pressure data for TCMTB and tebuconazole, as reported by Buckman Laboratories, Inc. and Mobay Corporation, are shown in Tables G-1 and G-2, respectively.

The Clausius-Clapeyron equation (Equation G-1) was used to correlate this data and used to calculate the enhancement factor in the Ziger and Eckert model.

$$\ln P^{vap} = A - \frac{B}{T} \qquad \text{G-1}$$

The two parameters, which are the slope and intercept from the plot of ln P^{vap} *vs* $1/T$ in Equation G-1, are (for P^{vap} in bar and T in K) :

for TCMTB $A = 13.30$

$B = 9642.14$

for tebuconazole $A = 28.03$

$B = 15740.09$

and the percent deviation defined by

$$\%\text{Deviation} = \left[\frac{P_{cal} - P_{exp}}{P_{exp}}\right] \times 100 \qquad \text{G-2}$$

is also shown in Table G-1 for TCMTB.

Table G-1 Vapor pressure of TCMTB reported by Buckman Labs Inc.

Temperature(K)	$P_{Experiment}$ (bar)	$P_{Calculate}$(bar)	% Deviation
293.15	3.25×10^{-9}	3.10×10^{-9}	-4.94
298.15	5.39×10^{-9}	5.38×10^{-9}	-0.25
323.15	5.33×10^{-8}	6.56×10^{-8}	18.78
323.15	7.92×10^{-8}	6.56×10^{-8}	-20.68
333.15	1.50×10^{-7}	1.61×10^{-7}	6.67
333.15	2.15×10^{-7}	1.61×10^{-7}	-33.78
343.15	2.83×10^{-7}	3.74×10^{-7}	24.24
343.15	4.92×10^{-7}	3.74×10^{-7}	-31.71

Table G-2 Vapor pressure of tebuconazole reported by Mobay Corp.

Temperature (K)	P (bar)
293.15	7.2×10^{-12}
393.15	4.5×10^{-9}