MODELING THE PHASE EQUILIBRIUM OF MULTICOMPONENT SYSTEMS

INVOLVING SOLIDS, SUPERCRITICAL FLUIDS, AND COSOLVENTS

by

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A project report submitted in partial fulfillment of the requirements for the degree of

MASTER OF ENGINEERING
in
CHEMICAL ENGINEERING

UNIVERSITY OF PUERTO RICO
MAYAGÜEZ CAMPUS
2006

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Abstract

Carbon dioxide is one of the most commonly used supercritical fluids. However, its uses are limited due to its low solubility capacity for polar substances. Addition of cosolvents improves the solubility of polar and non-polar solutes in CO_2. Many authors have used equations of state combined with mixing rules to develop mathematical models for the determination of solubilities of systems composed of a solute, a solvent, and a cosolvent.

In this work, the Peng-Robinson equation of state with the van der Waals mixing rules were used to formulate a mathematical model for the solubility of solids in supercritical fluids with cosolvents, i.e., in ternary systems. All three binary interaction parameters involved were determined for nine ternary systems for which experimental data were available (for a total of 22 isotherms); these parameters were used to calculate the solubilities for those systems. Results obtained showed that the model fitted very well the experimental data for all the systems studied.

Also, simulation runs were done varying the cosolvent concentration to evaluate the impact that it had in the systems under study. The practical use of this exercise is to know how much cosolvent to use in a given application. An increase of the cosolvent concentration improved significantly the solubility of the solutes in carbon dioxide except for 2-naphthol for which it was observed that, beyond a certain point, an increase in pressure or cosolvent concentration reduced the solubility of the solute in CO_2.

Resumen

Dióxido de carbono es uno de los fluidos supercríticos más comúnmente utilizado. Sin embargo, su uso está limitado debido a su poca capacidad de disolver sustancias polares. La adición de cosolventes mejora la solubilidad de solutos polares y no polares en CO_2. Muchos autores han usado ecuaciones de estado combinadas con reglas de mezclado para desarrollar modelos matemáticos para la determinación de las solubilidades de los sistemas compuestos de un soluto, un solvente y un cosolvente.

En este trabajo, la ecuación de estado de Peng-Robinson con las reglas de mezclado de van der Waals se utilizaron para formular un modelo matemático para la solubilidad de sólidos en fluidos supercríticos con cosolventes, esto es, en sistemas ternarios. Los tres parámetros de interacción binaria involucrados se determinaron para nueve sistemas ternarios para los que había datos disponibles (para un total de 22 isotermas); estos parámetros se usaron para calcular las solubilidades para estos sistemas. Los resultados obtenidos muestran que el modelo ajusta muy bien los datos experimentales para todos los sistemas estudiados.

Además, se hicieron simulaciones variando la concentración de cosolvente para evaluar el impacto que ésta tiene en los sistemas bajo estudio. El uso práctico de este ejercicio es saber cuánto cosolvente usar en una aplicación dada. Un aumento en la concentración de cosolvente mejoró significativamente la solubilidad de los solutos en dióxido de carbono excepto para 2-naftol, para el cual se observó que, más allá de cierto punto, un aumento en la presión o en la concentración del cosolvente reduce la solubilidad del soluto en CO_2.

To my father…

Acknowledgements

My special gratitude to Abbott Biotechnology Ltd. (ABL) personnel, specifically Greisha Ruiz and John McIntyre from the Process Engineering Group and Orlando Velázquez and Zuleika Rodríguez from the Validation Group, who always allowed me to make arrangements to attend classes and meetings on Campus.

Thanks to Dr. L. Antonio Estévez for his understanding, guidance, and advice during all this time. Also, I want to thanks the members of the graduate committee, Dr. David Suleiman and Dr. William Hernández, for accepting to be part of this project, and to Dr. Robert Ríos for taking from his time and accepting to be Representative of Graduate Studies.

To my father: thank you for always inculcating the desire to get a higher education, although this time you will not be physically with me at the time of getting the degree. I know that from the heaven you are very proud of me.

Finally, but not less important, to God for giving me the strength and courage to continue ahead no matter what the obstacles appeared on the road. Thanks for allowing me realize each of my dreams.

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a	attraction interaction term, [$m^6 \cdot Pa/mol^2$]
A	Antoine constant, [-]
$AVERR\%$	percentage average error, [-]
b	molecular volume term, [m^3/mol]
B	Antoine constant, [K]
f	fugacity, [Pa]
k	interaction parameter, [-]
n	number of points, [-]
OF	objective function, [-]
P	pressure, [Pa]
R	ideal gas constant, [$m^3 \cdot Pa/mol \cdot K$]
T	temperature, [K]
V	molar volume, [m^3/mol]
y	solubility, [-]
Z	compressibility factor, [-]

Greek Symbols

ϕ	fugacity coefficient, [-]
ω	acentric factor, [-]

Subscripts

c	critical
i	component i
j	component j
m	mixture
r	reduced

Superscripts

sat	saturation
sol	solid

1. INTRODUCTION

1.1   Motivation

In the last decades, supercritical fluid technology has become popular due to its advantages when compared to conventional processes. Some of these advantages are higher mass-transfer rates, reduced unit operations, and higher efficiency. Its applications include the areas of extraction (of food ingredients, flavors/fragrances, pharmaceutical/cosmetic actives, and pollutants), chromatography, particle design, microelectronics, and biological applications, among others.

A supercritical fluid (SCF) is described as a fluid in a temperature and pressure state above the critical point. SCFs have a high diffusivity that is comparable to that of a gas, and a high solvent capacity that is comparable to that of liquids (Fukushima, 2000). Carbon dioxide (CO_2) is the supercritical fluid most commonly used due to properties such as low critical pressure and temperature, low reactivity, high purity, and availability, but its applicability its limited when used with polar compounds. However, it has been found that the addition of small amounts of a suitable cosolvent (or modifier) can greatly enhance its solvent power (Li *et al.*, 2003).

1.2   Theory

1.2.1   Supercritical Fluids

Supercritical fluids are described as any substance above its critical temperature and critical pressure. The fluid is neither a gas nor a liquid and is best described as an intermediate to the two extremes. Figure 1 shows the region of the supercritical fluids.
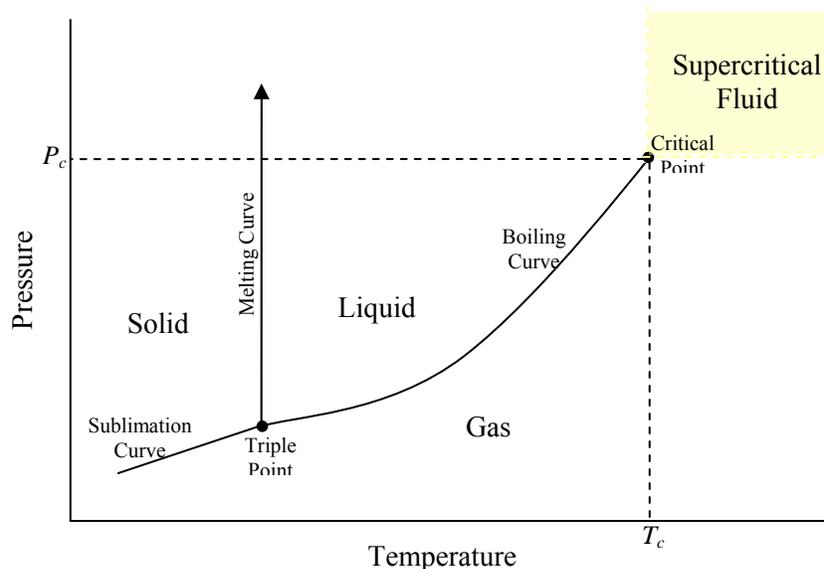
Figure 1. Phase Diagram for a Pure Substance

Supercritical fluids have an unusual combination of physical properties such as gas-like diffusivity and viscosity, zero surface tension, and liquid-like solvation and densities (Griffith *et al.*, 2001). Small changes in temperature or pressure near the critical point result in large changes in the density of the fluid that affects the solvent power. Some of the compounds most commonly used as supercritical fluids, and their critical properties, are shown in Table 1 (Williams and Clifford, 2000).

Table 1. Some substances used as supercritical fluids

Substance	T_c [K]	P_c [MPa]
carbon dioxide	304	7.4
water	647	22.1
ethane	305	4.9
ethene	282	5.0
propane	370	4.3
xenon	290	5.8
ammonia	406	11.4
nitrous oxide	310	7.2
fluoroform	299	4.9

1.2.2 Cosolvents

The addition of small amount of a third substance (cosolvent, entrainer, or modifier) can have dramatic effects on supercritical fluid phase behavior, especially if specific interactions between the cosolvent and one or more of the solutes exist (Ekart *et al.*, 1993). This phenomenon is known as the entrainer effect. An entrainer or cosolvent has a higher volatility than the solute. It can be a liquid, a solid, a gas, or a supercritical fluid (Ruckenstein and Shulgin, 2003).

1.2.3 Peng-Robinson Equation of State (EoS)

The Peng-Robinson EoS is considered one of the most popular cubic equations currently used in research, simulations, and optimizations in which thermodynamic and vapor-liquid-equilibrium (VLE) properties are required (Valderrama, 2003). It is given by

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{1.1}$$

where *a* is the attraction or cohesive parameter that is a function of the acentric factor and the reduced temperature. The *a* parameter has the following form

$$a\left(\omega, T_r\right) = a_c\, \alpha\left(\omega, T_r\right) \tag{1.2}$$

$$a_c = \frac{0.45724R^2T_c^2}{P_c} \tag{1.3}$$

$$\alpha(\omega, T_r) = \left[1 + \kappa(1 - \sqrt{T_r}\,)\right]^2 \tag{1.4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{1.5}$$

The *b* parameter is the covolume term (repulsive parameter) and has the following form

$$b = \frac{0.07780RT_c}{P_c} \tag{1.6}$$

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For mixtures, Equation (1.1) can be re-written as (Tester and Modell, 1997)

$$P = \frac{RT}{V_m - b_m} - \frac{a_m}{V_m(V_m + b_m) + b_m(V_m - b_m)} \tag{1.7}$$

Where the mixture parameters a_m and b_m are determined using mixing rules.

Equations (1.1) and (1.7) are in pressure-explicit form and are cubic in volume. They can be rewritten as a cubic equation (Peng and Robinson, 1976) as

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{1.8}$$

Where the dimensionless parameters A and B are

$$A = \frac{a_m P}{R^2 T^2} \tag{1.9}$$

$$B = \frac{b_m P}{RT} \tag{1.10}$$

Cubic equation (1.8) can be solved analytically. Details of the analytical solution of equation (1.8) are presented in Appendix A.

1.2.4 van der Waals Mixing Rule

The van der Waals (VDW) mixing rule is given by the following equations

$$a_m = \sum_i^n \sum_j^n y_i y_j a_{ij} \tag{1.11}$$

$$b_m = \sum_i^n \sum_j^n y_i y_j b_{ij} \tag{1.12}$$

for $i \neq j$

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{1.13}$$

$$b_{ij} = \frac{(b_{ii} + b_{jj})}{2} \tag{1.14}$$

for $i = j$

$$a_{ii} = a_i \qquad a_{jj} = a_j \qquad k_{ii} = k_{jj} = 0 \tag{1.15}$$

Substitution of equation (1.14) in equation (1.12) reduces the expression for b_m to the following

form

$$b_m = \sum_i^n y_i b_i \tag{1.16}$$

k_{ij} in the equation (1.13) is the so-called binary interaction parameter.

1.2.5 Solubility of Solids in SCFs

The solubility of the solid i in a supercritical fluid and cosolvent is determined by the

following equation

$$y_i = \left(\frac{P_i^{sat}}{P \phi_i} \right) \exp \left(V_i^{sol} \frac{P}{RT} \right) \tag{1.17}$$

where ϕ_i is the fugacity coefficient given by

$$\ln \phi_i = \ln \left(\frac{f_i}{y_i P} \right) = \left(\frac{-1}{RT} \right) \int_\infty^V \left[\left(\frac{\partial P}{\partial N} \right)_{T,V,N_j} - \frac{RT}{V} \right] dV - \ln Z \tag{1.18}$$

Evaluation of equation (1.18) gives (Müller *et al.*, 1989)

$$\ln \phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B} \left(\frac{2\sum_j^n x_j a_{ij}}{a} - \frac{b_i}{b} \right) \ln \left(\frac{Z + 2.414B}{Z - 0.414B} \right) \tag{1.19}$$

P_i^{sat} is the sublimation pressure normally given by a two-constant Antoine equation

$$\log P_i^{sat} = A - \frac{B}{T} \tag{1.20}$$

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and V_i^{sol}, P, T, and R are the solid molar volume, system pressure, system temperature, and the ideal gas constant, respectively.

1.3   Objectives

Many investigators have published equilibrium solubility data for various solids in SCFs; nevertheless, data for measurements on the equilibrium solubility of solids in SCFs with cosolvents are far from abundant. This research has been undertaken to evaluate the solubility behavior of systems involving solid, SCF, and cosolvent using a cubic EoS and a mixing rule. Peng-Robinson EoS and van der Waals mixing rules have been selected for this purpose. Estimated interaction parameters for the systems have been determined for different isotherms and the effect of the cosolvent concentration on the solubility has been evaluated.

2. LITERATURE REVIEW

In an effort to develop a model that can predict the solubility of solids in mixtures of supercritical fluids with cosolvents, several methods have been used by different investigators. These models include the use of equation of state (EoS) (e.g. Chafer *et al.*, 2004), solutions theories (e.g. Li *et al.*, 2004), expanded liquid model (e.g. Bae *et al.*, 2004), cluster solvation model (e.g. Cheng *et al.*, 2003), and density-based model (e.g. Jin *et al.*, 2004).

Models using EoS are based on relating the solubility to the pressure and the temperature through the fugacity coefficient evaluated from an EoS. Guha and Madras (2001), developed a model that combines the cubic Patel-Teja (PT) EoS with the Wong-Sandler (WS) mixing rule. The model was applied to correlate the solubilities of different ternary systems and the corresponding binaries. Only three empirical parameters were required to model the ternary systems which were the interaction parameter, the hypothetical infinite pressure activity coefficient, and the interactions between the two solutes. Based on the values of average absolute relative deviation (AARD) obtained they showed that the model was versatile to predict the solubility of binary and ternary polar and non-polar solutes.

Cháfer *et al.* (2004) used two types of thermodynamic models to calculate the solubility of quertecin in supercritical CO_2 and ethanol. One of the models used the group contribution (GC) EoS while the other used the Soave-Redlich-Kwong (SRK) EoS. They found that the SRK EoS has more capability to correlate the experimental solubility data but the predictions of the GC-EoS considerably improved when a pressure-dependent parameter was introduced in the model.

Huang *et al.* (2004) used the Peng-Robinson (PR) EoS to correlate the solubility data of cholesterol and cholesteryl benzoate in supercritical CO_2 in the presence of the polar cosolvents methanol and acetone. They pointed out that the equation has the advantage that it provides reasonable estimates of the complex solubility behavior of solids in supercritical CO_2 as a function of temperature and pressure once the required physical properties are known. The equation correlates well the experimental data of the systems. Berna *et al.* (2001) used the PR EoS and SRK EoS to correlate the solubility data for the system composed of catechin, CO_2, and ethanol. They found that both equations gave similar deviations at various conditions of pressure and temperature but the PR EoS showed better correlations with the experimental points. Cháfer *et al.* (2002) arrived to the same conclusion when they used the PR EoS and SRK EoS to correlate the solubility data for the system composed of epicatechin, CO_2, and ethanol.

Yang and Zhong (2005) combined the statistical associating fluid theory (SAFT) EoS with a one-parameter mixing rule to evaluate the capability of the SAFT approach for modeling the solubility of solid aromatic compounds in supercritical fluids with cosolvents. This model showed good agreement with the experimental observations with only one temperature dependent parameter. The results obtained were compared with the Peng-Robinson-Stryjek-Vera (PRSV) EoS combined with the van der Waals one parameter mixing rule, and it was found that the model provides better results than the cubic EoS. The model showed to be useful for the modeling of solids in supercritical fluids with cosolvents.

Bae *et al.* (2004) estimated the solubility of a ternary mixture consisting of supercritical fluid, solute, and cosolvent using an expanded liquid model (Flory-Huggins theory) that considered the supercritical fluid as a liquid phase. The model allows the prediction of the effect of the cosolvent concentration on the solubility of the solute in a supercritical mixed solvent.

Another model for the solubility of solids in supercritical fluid with and without cosolvents (for binary and ternary systems) using the solution theory was proposed by Li *et al*. (2004). For the ternary system, the model has four adjustable parameters which are related to the interactions between the molecules in the solution. The model showed better accuracy when compared with the hard-sphere van der Waals 1 (HSVDW1) and hard-sphere van der Waals 2 (HSVDW2) models. However, it is argued in the literature that using regular solution theory to predict the solubility of a solute is only a qualitative approach.

Other models that have been published in the literature include a simplified cluster solvation model by Cheng *et al*. (2003). Based on studies that reported the formation of clusters or aggregates of the solvent molecules around the solute at high-pressure conditions, they conclude that these clusters should be considered in solid solubility calculations. Therefore, they presented a model that has two temperature independent binary parameters to calculate the solid solubility for binary, multicomponent, and cosolvent systems with various supercritical fluids. For the case of cosolvent, they found that the calculation results were in satisfactory agreement with the experimental data.

Jin *et al.* (2004) used the modified Chrastil equation to correlate the solubilities of benzoic acid in supercritical CO_2 with pure cosolvents and mixed cosolvents. The Chrastil eqution is a density-based model that assumes that the solute is associated with the solvent to form a solvated complex and, when cosolvents are added into the system, the molecular interactions of the components become more complex. Jin *et al.* used a modification of the Chrastil equation that considered the formation of the solute/cosolvent/solvent complexes and obtained an equation to correlate the solubility of solids and liquids in supercritical CO_2 with cosolvents and mixed cosolvents. They found that the effect on the solubility of each mixed

cosolvent lies between those of the two pure cosolvents. When the correlated results were compared to the experimental data, a good agreement was found between them. Similar results were found when the modified Chrastil model was used by Jin *et al.* (2005) for the measurement of the solubility of propyl *p*-hydroxybenzoate in supercritical CO_2 with pure cosolvents and mixed cosolvents. The effect on the solubility of the mixed cosolvents lies between those of the pure cosolvents.

Another density-based model is that of Méndez-Santiago and Teja. Méndez-Santiago and Teja (2000), indicated that the models based on EoS are of limited utility in separation process design due to the fact the these models require several adjustable parameters to correlate data and they can seldom be used for extrapolation. They proposed a model to determine the solubility based on the dilute solution theory for ternary mixtures. Their study demonstrated that the model was capable of correlating data over a range of temperatures, solvent densities, and cosolvent concentrations. The model used only three parameters which were independent of temperature, pressure, and cosolvent concentration. Graphically the model can be represented as a single line. Sauceau *et al.* (2003) used the Méndez-Santiago and Teja model and the Chrastil model to correlate solubility data. They correlated the experimental equilibrium solubility data of the pharmaceutical solids in supercritical CO_2 with cosolvents and they found that it can be applied only to mixtures at constant composition while a good representation of the data was obtained with the Méndez-Santiago and Teja. Thakur and Gupta (2005) modified the Méndez-Santiago and Teja model because the original expression did not yield a satisfactory fit to their solubility data for griseofulvin in CO_2 with menthol as cosolvent. With the modified model, they obtained a good agreement between the correlated solubilities and the experimental data.

As can be seen, several investigators have studied the solubility of systems consisting of solid, SCF, and cosolvents, and different models have been proposed been the most popular ones those based on various EoS. While most of the works cited in this section focus only on their own system, this investigation will focus in the use of one of the models that are based on the EoS in conjunction with a mixing rule to determine the solubility of several systems.

3. METHODOLOGY

This section describes the method followed to determine the solubility of the systems selected for this research, to estimate the interaction parameters, and to evaluate the effect of the cosolvent concentration on solubility. Data used to achieve the objectives of this work are also presented. Throughout this work, the term solubility refers to the solute mole fraction in the saturated SCF phase.

3.1   Method

For each of the systems studied, the solubility was determined using a model based in the Peng-Robinson EoS (Equation 1.1) and the van der Waals mixing rules (Equations 1.11 and 1.12) at different temperatures and pressures. An objective function (OF) was defined and minimized to estimate parameters for all binary interactions between the solute, solvent, and cosolvent at a particular temperature (isotherm). The objective function defined as the root mean square of the absolute deviation between the calculated and experimental solubilities was used in this work. The expression for the objective function is

$$OF = \sqrt{\frac{\sum_{i=1}^{N_p}\left(y_{i,calculated} - y_{i,experimental}\right)^2}{N_p}} \qquad (3.1)$$

where y is the solubility of the solute in the solvent and cosolvent and N_p is the number of experimental points for each isotherm. The values for the experimental solubilities were taken from literature.

The objective function was minimized using the *Solver* tool of Microsoft Excel®. This tool is an iterative search routine and was used to estimate the interaction parameters. The

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interaction parameters at each isotherm studied were estimated by minimizing the objective function given by Equation 3.1. To appreciate the quality of the fit graphically, the estimated interaction parameters were used to determine the solubility of the solute at different cosolvent concentrations for an isotherm. The quality of the fit by the model was assessed by the percent average error, AVERR%, defined as:

$$AVERR\% = \frac{\sqrt{\dfrac{\sum_{i=1}^{N_p}(y_{i,calculated} - y_{i,experimental})^2}{N_p}}}{\overline{y}_{experimental}} 100 = \frac{(OF)(N_p)}{\sum_{i=1}^{N_p} y_{i,experimental}} 100 \qquad (3.2)$$

3.2   Data

Nine systems were studied, which are summarized in Table 2. The physical properties of solutes and solvents are listed in Table 3 and Table 4, respectively, and their structures are shown in Table 5.

Table 2. Systems analyzed

Solid	Solvent	Cosolvent	Cosolvent Concentration (mole percent)	P [MPa]	T [K]	Reference
anthracene	CO_2	acetone	4	10 - 30	308.1 318.1 328.1	[1]
anthracene	CO_2	ethanol	4	10 - 30	308.1 318.1 328.1	[1]
anthracene	CO_2	cyclohexane	4	10 - 30	308.1 318.1 328.1	[1]
2-naphthol	CO_2	acetone	3.6	10 - 30	308.1 318.1 328.1	[1]

Table 2. Systems analyzed (Cont.)

Solid	Solvent	Cosolvent	Cosolvent Concentration (mole percent)	P [MPa]	T [K]	Reference
2-naphthol	CO_2	ethanol	3.6	10 - 30	308.1 318.1 328.1	[1]
2-naphthol	CO_2	cyclohexane	3.6	10 - 30	308.1 318.1 328.1	[1]
benzoic acid	CO_2	ethanol	2	8 - 23	328.15	[2]
benzoic acid	CO_2	ethyl acetate	2	8 - 23	328.15	[2]
aspirin	CO_2	acetone	3	10 - 20	318.15 328.15	[3]

[1] Li *et al.*, 2003
[2] Jin *et al.*, 2004
[3] Huang *et al.*, 2004

Table 3. Solutes physical properties

Substance	P_c [MPa]	T_c [K]	ω	V^{sol} [m³/mol]	A	B [K]	P^{sat} [Pa]	Ref.
anthracene	3.12	869.30	0.3531	0.0001426	12.147	4397.6	---	[4]
benzoic acid	4.50	752.00	0.6200	0.0000965	14.408	4618.1	---	[4]
2-naphthol	4.29	825.15	0.460	0.0001127 [5]	14.815	4923.9	---	[6]
aspirin	3.28	762.9	0.818	0.00012964	---	---	0.2803 @ 318.15 K 0.8011 @ 328.15 K	[7]

[4] Caballero *et al.*, 1992
[5] Cheng *et al.*, 2003
[6] Škerget *et al.*, 2002
[7] Huang *et al.*, 2004

Table 4. Solvents physical properties

Substance	P_c [MPa]	T_c [K]	ω	Reference
CO_2	7.374	304.12	0.225	[8]
acetone	4.700	508.10	0.307	[8]
ethanol	6.148	513.92	0.649	[8]
cyclohexane	4.073	553.50	0.211	[8]
ethyl acetate	3.830	523.20	0.361	[8]

[8] Poling *et al.*, 2001

Table 5. Substance structures

Name	Structure	Type of Substance
anthracene		solid
2-naphthol	OH	solid
benzoic acid	$\overset{O}{\underset{\|\|}{}}$ C-OH	solid
aspirin	$\overset{O}{\underset{\|\|}{}}$ C-OH, CH_3-C	solid
acetone	CH_3-$\overset{O}{\underset{\|\|}{C}}$-$CH_3$	cosolvent
ethanol	CH_3-CH_2-OH	cosolvent
cyclohexane		cosolvent
ethyl acetate	CH_3-$\overset{O}{\underset{\|\|}{C}}$-O-$CH_2$-$CH_3$	cosolvent
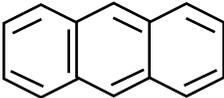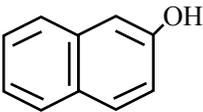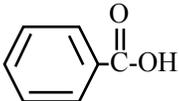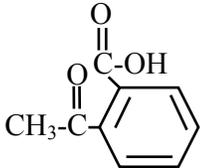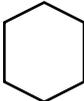
4. RESULTS

4.1   Modeling Solubilities

Table 6 shows the estimated interaction parameters for the different systems analyzed. The minimized values for the objective function are also presented in the table.   The experimental solubilities used for the determination of the interaction parameters are shown in Table 7 in the Appendix B.

Figure 2 shows the solubility behavior at one temperature, 318.1 K, of the system anthracene-CO_2 with three different cosolvents and with no cosolvent; therefore, the effect of the cosolvent is shown. The cosolvents used are acetone, ethanol, and cyclohexane, all at a mole fraction of 4 %. Experimental values are compared to those calculated using the Peng-Robinson EoS and van der Waals mixing rule. To show the general trend of EoS predictions, the whole solubility range is shown here, i.e., five log cycles. A similar behavior was observed for the rest of the systems covered in this work.

Figure 3 is exactly the same as Figure 2 except that only two log cycles are shown in the solubility scale to better appreciate the solubility behavior. Comparisons between experimental and calculated solubility for other systems and other temperatures are shown in Appendix C.

Figure 4 shows the effect of temperature on the solubility for the system anthracene-CO_2-acetone using the calculated solubility data with Peng-Robinson EoS and the calculated interaction parameters.

Table 6. Computed interaction parameters

Solid (2)	Solvent (1)	Cosolvent (3)	Cosolvent Concentration (mole percent)	N_p	T [K]	k_{12} [a]	k_{13} [a]	k_{23} [a]	Objective Function	AVERR%
anthracene	CO_2	acetone	4	5	308.1	0.11881	0.04049	-0.04956	4.68239E-06	5.62
				5	318.1	0.10277	-0.02907	0.08561	3.66211E-06	3.79
				5	328.1	0.10467	-0.08849	0.09852	6.27203E-06	6.37
anthracene	CO_2	ethanol	4	5	308.1	0.12136	0.11386	-0.10865	6.67008E-06	6.24
				5	318.1	0.10317	-0.02646	0.06489	8.52919E-06	7.67
				5	328.1	0.09708	-0.10090	0.14181	8.20096E-06	7.12
anthracene	CO_2	cyclohexane	4	5	308.1	0.11608	0.09803	-0.11724	7.31166E-06	5.84
				5	318.1	0.10216	0.00636	0.01520	6.96943E-06	5.57
				5	328.1	0.08904	-0.08355	0.12497	7.69342E-06	5.90
benzoic acid	CO_2	ethanol	2	6	328.15	-0.04469	-0.01222	-0.00315	0.00275	28.39
benzoic acid	CO_2	ethyl acetate	2	6	328.15	0.00898	0.00384	0.00198	0.00017	7.04
2-naphthol	CO_2	acetone	3.6	6	308.1	0.03435	-0.33838	0.40086	2.33054E-05	3.38
					318.1	0.06726	-0.26177	-0.00178	1.28637E-05	1.27
					328.1	0.06709	-0.24317	-0.16232	2.7E-05	1.81
2-naphthol	CO_2	ethanol	3.6	6	308.1	-0.02992	-0.60838	0.47671	1.66205E-05	0.70
					318.1	0.01360	-0.40690	0.17792	0.00012	5.24
					328.1	0.01741	-0.29615	0.28703	7.44994E-05	3.48
2-naphthol	CO_2	cyclohexane	3.6	6	308.1	0.02888	-0.41440	0.19366	7.57201E-06	0.75
					318.1	0.02430	-0.23423	0.34543	2.95057E-05	2.62
					328.1	0.04349	-0.16564	0.21044	3.69594E-05	2.93
aspirin	CO_2	acetone	3	5	318.15	0.18065	0.00736	-0.00399	1.77616E-05	4.18
					328.15	0.17690	-0.07141	0.01565	1.53E-05	3.32

[a] 12 refers to the solvent/solute, 13 refers to the solvent/cosolvent, and 23 refers to the solute/cosolvent.
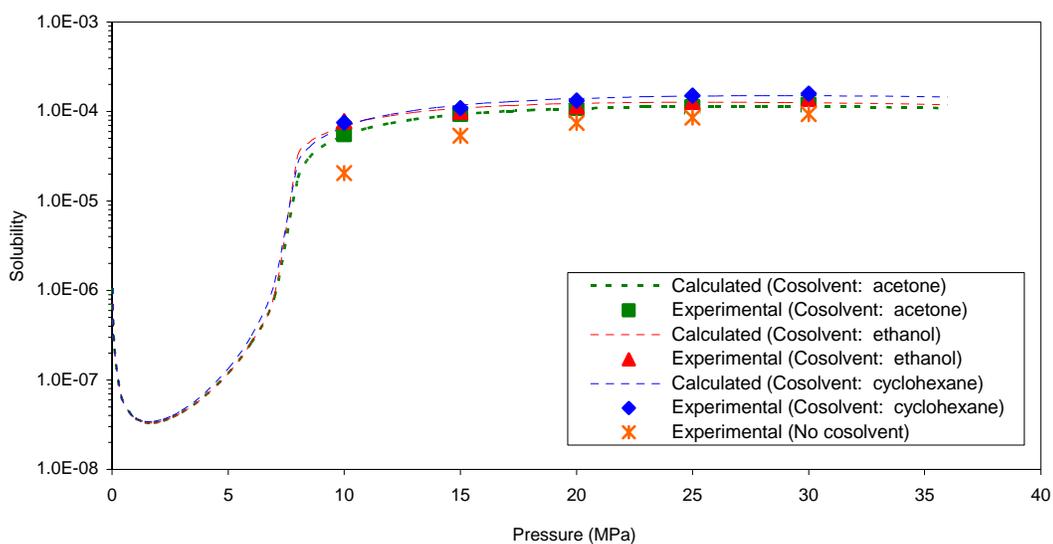
Figure 2. Behavior of the system anthracene in CO_2 and three different cosolvents at 318.1 K using the Peng-Robinson EoS. Cosolvent mole fraction: 4%.
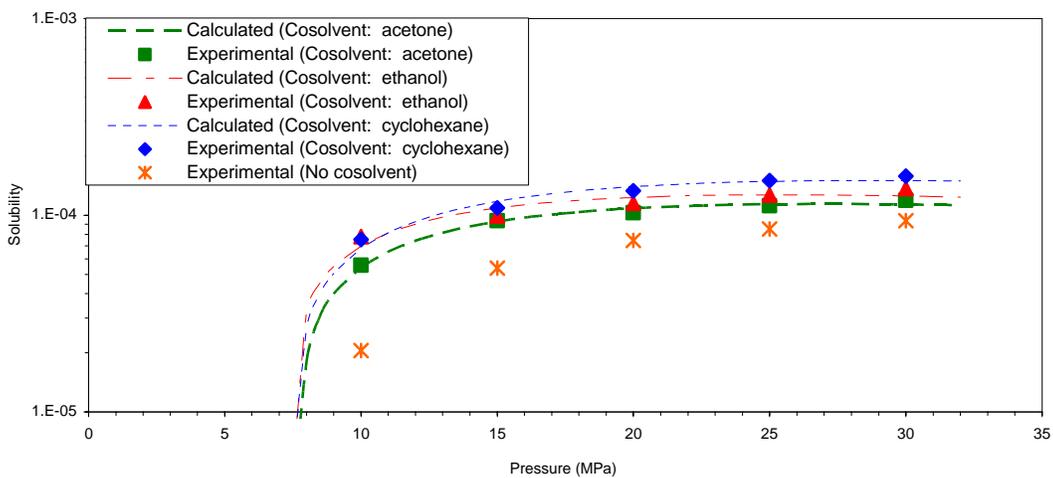
Figure 3. Comparison between calculated and experimental data for the system anthracene in CO_2 and three different cosolvents at 318.1 K. Cosolvent mole fraction: 4%.
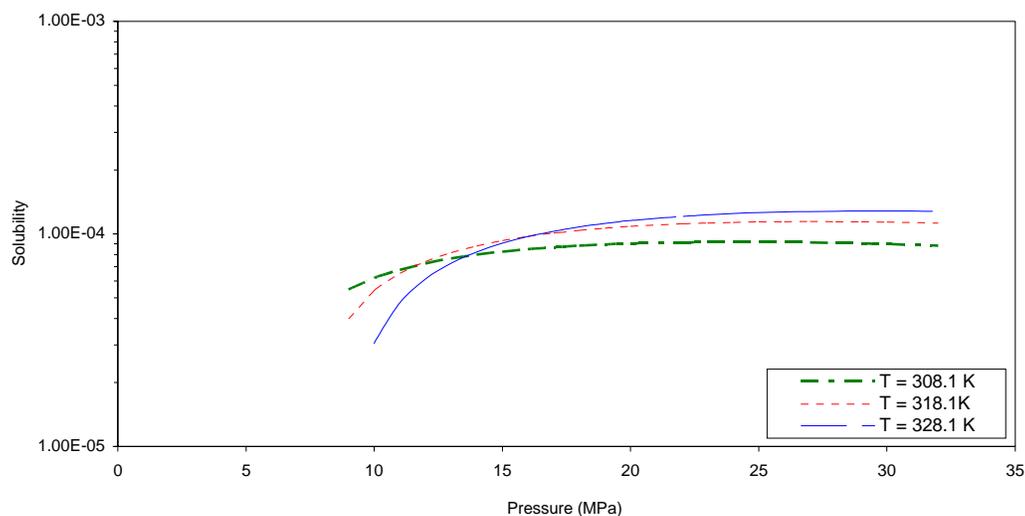
Figure 4. Effect of temperature on the solubility for the system anthracene-CO_2-acetone.

4.2   Variation of Cosolvent Concentration

As explained in section 1.2, the addition of small amount of a cosolvent can have a marked effect on the supercritical fluid phase behavior and on the solubility of the solute.   Since the systems presented in Table 2 are for a specific cosolvent concentration, the effect that the variation of cosolvent concentration has on the solubility at a constant temperature and different pressures was analyzed.   This simulation exercise is of practical interest because it allows determining the amount of cosolvent in a given application.

Once the estimated interaction parameters, k_{ij}, for each of the different systems were determined, they were used along with the Peng-Robinson EoS and vdW mixing rules to model for each system the solubility at different cosolvent concentrations. The information obtained was presented in a plot of solubility versus concentration so as to appreciate the effect of the

cosolvent concentration variation on the solubility. The cosolvent concentration was varied within the mole fraction range of 0 % (no cosolvent) to 40 %.

For the system anthracene and supercritical CO_2 with acetone as cosolvent the effect of the variation of the cosolvent concentration at 318.1 K is presented in Figure 5. Five lines are presented there corresponding to five different pressures from 10 MPa to 30 MPa. Results for other systems are shown in Appendix D.

It should be pointed out that one of the uses of knowing the effect of the cosolvent concentration on the solubility is that it provides information or insight on the amount of cosolvent needed to obtain a particular solubility result.
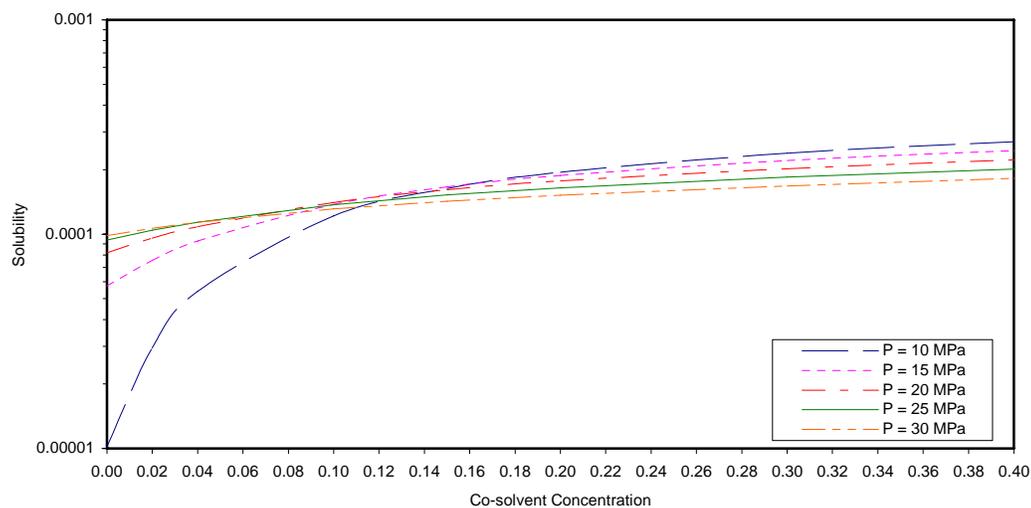
Figure 5. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and acetone as cosolvent at 318.1 K.

5. DISCUSSION

5.1   Modeling Solubilities

For the system anthracene and CO_2 with acetone, ethanol, and cyclohexane as cosolvents at 318.1 K, Figure 3 shows that the calculated interaction parameters yield good agreement between the calculated and experimental solubility data.   The Peng-Robinson EoS fits the experimental data very well because, as shown in Table 6, the values obtained for the AVERR% were as low as 3.79% and all below 7.67%. Similar results were observed for the other systems studied where AVERR% values from less than 1% to 7% were obtained except for the system composed of benzoic acid, CO_2, and ethanol. For this system AVERR% was 28.39% which should be considered high if it is compared with the other systems studied. This high AVERR% is probably due to unusually high experimental errors.

When the interaction parameter for the solute-solvent, k_{12}, is inspected in Table 6, it can be observed that for the systems anthracene-CO_2 and aspirin-CO_2 the value is approximately constant when compared to the second decimal place. Therefore, the interaction parameter k_{12} should be considered independent of temperature over the temperature range shown in Table 6. However, for the system 2-naphthol-CO_2 the value of k_{12} was found dependent on temperature.

For each isotherm studied the solubility increases as the pressure increases.   The isotherms show that the solubility of the solute in CO_2 was improved when the cosolvent was added. The isotherms also showed that the type of cosolvent used has an impact on the solute solubility. For the case of anthracene, the cosolvent strength increases as follow: cyclohexane > ethanol > acetone. The solubility of anthracene, which is a non-polar solute, was higher with the non-polar cosolvent cyclohexane than with the polar cosolvents ethanol and acetone.   This pattern was observed in anthracene at all the temperatures studied. For the other systems, it was

found that for 2-naphthol the cosolvent effect was highest for ethanol; for benzoic acid the cosolvent effect was also highest for ethanol.

The effect of ethanol over 2-naphthol and benzoic acid could be explained due to the fact that both solutes are polar substances and the ethanol is also a polar substance. As explained by Ting *et al.* (1993), when using a polar cosolvent for polar solutes, the largest increase in solubility would be expected to be a result of specific chemical interactions like hydrogen bonding or charge transfer complex formation.

The temperature has an effect on the solubility of the solute in CO_2. For the systems studied in this work, it was observed that at low pressures (between approximately 5 to 15 MPa), an increase of temperature adversely affects the solubility since it is reduced. However, there is a crossover point beyond which an increase of temperature improves the solute solubility. This effect is shown in Figure 4 for the system anthracene-CO_2-acetone at temperatures of 308.1 K, 318.1 K, and 328.1 K where the highest solubilities were obtained at the highest temperature and pressures above approximately 15 MPa. Jin *et al.* (2004) explained that the enhancement of solubility at high pressures and temperatures may be caused by the fact that the vapor pressure of the solute and the intermolecular interactions between the solute and the cosolvent play an important role at high temperatures. This is in agreement with the analysis of Chimowitz and Pennisi (1986) who indicated that an accepted explanation for this phenomenon is that at pressures below the crossover pressure, the density of the gas is more sensitive to temperature changes than at higher pressures (an increase in temperature produces a reduction in density and hence in solubility); at higher pressures, above the crossover point, the vapor-pressure effect is more important than the density effect (an increase in temperature produces an increase in vapor pressure and hence in solubility).

5.2 Effect of Variation of Cosolvent Concentration

For the system of anthracene in CO_2 with acetone as cosolvent at 318.1 K, Figure 5 shows that the solubility increases with the cosolvent concentration. For each line shown in Figure 5, there is one experimental point that corresponds to the solubility at a cosolvent concentration of 4 % mole fraction. It can be noted that, for cosolvent concentrations up to approximately 0.1 mole fraction (10 %), the solubility increases with the cosolvent concentration and the system pressure. However, this behavior changes for cosolvent concentrations above 0.1 mole fraction. Beyond this point the solubility increases with the cosolvent concentration but decreases with the system pressure. This type of behavior was observed for the systems that involve anthracene at all temperatures, except at 328.1 K, with ethanol and cyclohexane as cosolvents. The same behavior was also observed for benzoic acid in CO_2 with ethanol as cosolvent. For 2-naphthol and aspirin a different behavior was observed. The plots are presented in Appendix D.

At 328.1 K the solubility increases with an increase in cosolvent concentration or an increase in the pressure but at some point the solubility begins to drop with increase of concentration or increase of pressure. This behavior corresponds to anthracene in CO_2 with ethanol or cyclohexane as cosolvents. For benzoic acid in CO_2 with ethyl acetate as cosolvent and aspirin in CO_2 with acetone as cosolvent is directly proportional to the cosolvent concentration and to the system pressure. It was observed that the solubility of 2-naphthol, in most cases, decrease with increasing pressure or cosolvent concentration beyond a certain point.

6. CONCLUSIONS AND RECOMMENDATIONS

The Peng-Robinson EoS and the vdW mixing rules model were used to determine solubilities of systems that involved solid, supercritical fluid, and cosolvent. A good agreement was found between the experimental solubility data and the solubilities calculated with the model. The solubility of the systems was influenced by the pressure and temperature. For temperature, there was a crossover point below which the solubility decreased with temperature. Increasing the temperature enhanced the solute solubility in CO_2 at pressures beyond the crossover point. The solubility increased with pressure in all cases (within the experimental ranges of the data).

The effect of the variation of the cosolvent concentration was evaluated. It was found that the solubility increases with the cosolvent concentration except for 2-naphthol. For this system, it was observed that at certain point, increasing in pressure or cosolvent concentration decreased the solubility of the solute in CO_2.

The general conclusions of this work depend largely on the type of interactions between the solute and both the solvent and cosolvent. Although the available ternary data are not abundant, there are some that were not included in this report mainly because not all required properties were available for the solid. The missing properties were mostly critical properties or vapor pressure. These can be estimated but that was beyond the scope of this report. Therefore, it is recommended to estimate such properties and to extend this study to as many ternary systems as possible. It is also recommended to extend this study to other EoS and/or mixing rule to determine how the experimental data fit other models.

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APPENDICES

Appendix A

Analytical Solution for the Roots of a Cubic Polynomial

Peng-Robinson EoS can be written in the form of equation (1.8) which has the following form

$$x^3 + p_1 x^2 + p_2 x + p_3 = 0 \tag{A.1}$$

Tester and Modell (1997), provides the solution for cubic equations with the form of equation (A.1). For this type of equation there will be three roots, x_1, x_2, and x_3. The values of these roots will depend on the value of the discriminant D^*.

The discriminant is defined as

$$D^* \equiv Q^3 + R^2 \tag{A.2}$$

with

$$Q \equiv \frac{3p_2 - p_1^2}{9} \tag{A.3}$$

$$R \equiv \frac{9p_1 p_2 - 27 p_3 - 2p_1^3}{54} \tag{A.4}$$

For $D^* > 0$, there are one (1) real root, x_1, and two (2) imaginary roots, x_2 and x_3, given by

$$x_1 = S + T - \frac{1}{3} p_1 \tag{A.5}$$

$$x_{2,3} = -\frac{1}{2}(S + T) - \frac{1}{3} p_1 \pm \frac{1}{2} i\sqrt{3}(S - T) \tag{A.6}$$

$$S = \left(R + \sqrt{D^*}\right)^{1/3} \tag{A.7}$$

$$T = \left(R - \sqrt{D^*}\right)^{1/3} \tag{A.8}$$

For $D^* = 0$, $S = T$

For $D^* < 0$, there are three (3) real roots, x_1, x_2, and x_3, given by

$$x_1 = 2\sqrt{-Q}\cos\left(\frac{\theta}{3}\right) - \frac{1}{3}p_1 \tag{A.9}$$

$$x_2 = 2\sqrt{-Q}\cos\left(\frac{\theta}{3} + 120°\right) - \frac{1}{3}p_1 \tag{A.10}$$

$$x_3 = 2\sqrt{-Q}\cos\left(\frac{\theta}{3} + 240°\right) - \frac{1}{3}p_1 \tag{A.11}$$

$$\cos(\theta) = \frac{R}{\sqrt{-Q^3}} \tag{A.12}$$

In the vapor-liquid region, only the largest and the smallest roots are significant. The largest root represents the vapor phase while the smallest root represents the liquid phase. The middle root is in a region of intrinsic instability.

Appendix B

Experimental Solubility Data

Table 7 presents the experimental solubilities, $y_{experimental}$, for the different systems studied. Experimental solubilities were used to determine the values of the interaction parameters and the AVERR% showed in Table 6. Table 7 also presents the experimental solubility data for the binary systems.

Table 7. Experimental solubility data

Solid	Solvent	Cosolvent	Cosolvent Concentration (mole percent)	N_p	T [K]	P [MPa]	$y_{experimental}$	Reference
anthracene	CO_2	acetone	4	5	308.1	10.0	6.66×10^{-5}	[1]
						15.0	7.68×10^{-5}	
						20.0	8.59×10^{-5}	
						25.0	9.16×10^{-5}	
						30.0	9.56×10^{-5}	
anthracene	CO_2	acetone	4	5	318.1	10.0	5.57×10^{-5}	[1]
						15.0	9.39×10^{-5}	
						20.0	10.3×10^{-5}	
						25.0	11.2×10^{-5}	
						30.0	11.9×10^{-5}	
anthracene	CO_2	acetone	4	5	328.1	10.0	3.68×10^{-5}	[1]
						15.0	8.68×10^{-5}	
						20.0	10.6×10^{-5}	
						25.0	12.8×10^{-5}	
						30.0	13.5×10^{-5}	
anthracene	CO_2	ethanol	4	5	308.1	10.0	8.51×10^{-5}	[1]
						15.0	9.92×10^{-5}	
						20.0	10.9×10^{-5}	
						25.0	11.6×10^{-5}	
						30.0	12.5×10^{-5}	

Table 7. Experimental solubility data (Cont.)

Solid	Solvent	Cosolvent	Cosolvent Concentration (mole percent)	N_p	T [K]	P [MPa]	$y_{experimental}$	Reference
anthracene	CO_2	ethanol	4	5	318.1	10.0	7.78×10^{-5}	[1]
						15.0	9.93×10^{-5}	
						20.0	11.5×10^{-5}	
						25.0	12.7×10^{-5}	
						30.0	13.7×10^{-5}	
anthracene	CO_2	ethanol	4	5	328.1	10.0	5.22×10^{-5}	[1]
						15.0	9.88×10^{-5}	
						20.0	12.7×10^{-5}	
						25.0	14.4×10^{-5}	
						30.0	15.4×10^{-5}	
anthracene	CO_2	cyclohexane	4	5	308.1	10.0	9.22×10^{-5}	[1]
						15.0	11.1×10^{-5}	
						20.0	13.0×10^{-5}	
						25.0	14.2×10^{-5}	
						30.0	15.1×10^{-5}	
anthracene	CO_2	cyclohexane	4	5	318.1	10.0	7.54×10^{-5}	[1]
						15.0	10.9×10^{-5}	
						20.0	13.3×10^{-5}	
						25.0	15.0×10^{-5}	
						30.0	15.8×10^{-5}	
anthracene	CO_2	cyclohexane	4	5	328.1	10.0	5.60×10^{-5}	[1]
						15.0	11.1×10^{-5}	
						20.0	14.3×10^{-5}	
						25.0	16.4×10^{-5}	
						30.0	17.8×10^{-5}	
benzoic acid	CO_2	ethanol	2	6	328.15	8.0	0.3659×10^{-3}	[2]
						11.0	3.9340×10^{-3}	
						13.0	8.0922×10^{-3}	
						17.0	13.594×10^{-3}	
						20.0	15.305×10^{-3}	
						23.0	16.821×10^{-3}	

Table 7. Experimental solubility data (Cont.)

Solid	Solvent	Cosolvent	Cosolvent Concentration (mole percent)	N_p	T [K]	P [MPa]	$y_{experimental}$	Reference
benzoic acid	CO_2	ethyl acetate	2	6	328.15	8.0	0.1205×10^{-3}	[2]
						11.0	0.6421×10^{-3}	
						13.0	1.0725×10^{-3}	
						17.0	3.3353×10^{-3}	
						20.0	4.2538×10^{-3}	
						23.0	4.8961×10^{-3}	
2-naphthol	CO_2	acetone	3.6	6	308.1	10.05	4.83×10^{-4}	[1]
						14.0	5.85×10^{-4}	
						18.0	6.35×10^{-4}	
						22.05	7.06×10^{-4}	
						26.0	8.16×10^{-4}	
						30.0	9.16×10^{-4}	
2-naphthol	CO_2	acetone	3.6	6	318.1	10.05	4.78×10^{-4}	[1]
						14.0	7.66×10^{-4}	
						18.0	9.77×10^{-4}	
						22.05	11.0×10^{-4}	
						26.0	12.6×10^{-4}	
						30.0	15.0×10^{-4}	
2-naphthol	CO_2	acetone	3.6	6	328.1	10.05	3.79×10^{-4}	[1]
						14.0	10.7×10^{-4}	
						18.0	15.0×10^{-4}	
						22.05	18.7×10^{-4}	
						26.0	22.3×10^{-4}	
						30.0	19.0×10^{-4}	
2-naphthol	CO_2	ethanol	3.6	6	308.1	10.05	18.2×10^{-4}	[1]
						14.0	21.7×10^{-4}	
						18.0	23.6×10^{-4}	
						22.05	25.3×10^{-4}	
						26.0	26.8×10^{-4}	
						30.0	27.7×10^{-4}	
2-naphthol	CO_2	ethanol	3.6	6	318.1	10.05	11.5×10^{-4}	[1]
						14.0	20.6×10^{-4}	
						18.0	23.6×10^{-4}	
						22.05	25.7×10^{-4}	
						26.0	27.5×10^{-4}	
						30.0	30.2×10^{-4}	

Table 7. Experimental solubility data (Cont.)

Solid	Solvent	Cosolvent	Cosolvent Concentration (mole percent)	N_p	T [K]	P [MPa]	$y_{experimental}$	Reference
2-naphthol	CO_2	ethanol	3.6	6	328.1	10.05	5.53×10^{-4}	[1]
						14.0	14.9×10^{-4}	
						18.0	21.6×10^{-4}	
						22.05	24.3×10^{-4}	
						26.0	29.3×10^{-4}	
						30.0	32.7×10^{-4}	
2-naphthol	CO_2	cyclohexane	3.6	6	308.1	10.05	7.33×10^{-4}	[1]
						14.0	8.84×10^{-4}	
						18.0	9.74×10^{-4}	
						22.05	10.6×10^{-4}	
						26.0	11.4×10^{-4}	
						30.0	12.4×10^{-4}	
2-naphthol	CO_2	cyclohexane	3.6	6	318.1	10.05	5.80×10^{-4}	[1]
						14.0	8.51×10^{-4}	
						18.0	10.7×10^{-4}	
						22.05	13.3×10^{-4}	
						26.0	13.8×10^{-4}	
						30.0	15.5×10^{-4}	
2-naphthol	CO_2	cyclohexane	3.6	6	328.1	10.05	3.13×10^{-4}	[1]
						14.0	8.93×10^{-4}	
						18.0	12.2×10^{-4}	
						22.05	14.6×10^{-4}	
						26.0	17.8×10^{-4}	
						30.0	18.9×10^{-4}	
aspirin	CO_2	acetone	3	5	318.15	10.0	0.218×10^{-3}	[3]
						12.0	0.337×10^{-3}	
						15.0	0.428×10^{-3}	
						17.2	0.525×10^{-3}	
						20.0	0.615×10^{-3}	
aspirin	CO_2	acetone	3	5	328.15	10.0	0.113×10^{-3}	[3]
						12.0	0.321×10^{-3}	
						15.0	0.498×10^{-3}	
						17.2	0.612×10^{-3}	
						20.0	0.757×10^{-3}	

Table 7. Experimental solubility data (Cont.)

Solid	Solvent	Cosolvent	Cosolvent Concentration (mole percent)	N_p	T [K]	P [MPa]	$y_{experimental}$	Reference
aspirin	CO_2	None	0	8	318.15	12.0	0.72×10^{-4}	[3]
						15.0	1.39×10^{-4}	
						17.2	1.75×10^{-4}	
						18.5	1.95×10^{-4}	
						20.0	2.12×10^{-4}	
						21.5	2.28×10^{-4}	
						23.0	2.34×10^{-4}	
						25.0	2.58×10^{-4}	
aspirin	CO_2	None	0	8	328.15	12.0	0.63×10^{-4}	[3]
						15.0	1.37×10^{-4}	
						17.2	1.82×10^{-4}	
						18.5	2.34×10^{-4}	
						20.0	2.77×10^{-4}	
						21.5	2.86×10^{-4}	
						23.0	3.03×10^{-4}	
						25.0	3.47×10^{-4}	
2-naphthol	CO_2	None	0	6	308.1	10.05	2.49×10^{-4}	[1]
						14.00	4.33×10^{-4}	
						18.00	5.09×10^{-4}	
						22.05	5.47×10^{-4}	
						26.00	6.10×10^{-4}	
						30.00	6.54×10^{-4}	
2-naphthol	CO_2	None	0	6	318.1	10.05	1.48×10^{-4}	[1]
						14.00	4.70×10^{-4}	
						18.00	6.49×10^{-4}	
						22.05	7.72×10^{-4}	
						26.00	8.47×10^{-4}	
						30.00	9.64×10^{-4}	
2-naphthol	CO_2	None	0	6	328.1	10.05	1.16×10^{-4}	[1]
						14.00	4.41×10^{-4}	
						18.00	6.92×10^{-4}	
						22.05	9.25×10^{-4}	
						26.00	11.4×10^{-4}	
						30.00	12.3×10^{-4}	

Table 7. Experimental solubility data (Cont.)

Solid	Solvent	Cosolvent	Cosolvent Concentration (mole percent)	N_p	T [K]	P [MPa]	$y_{experimental}$	Reference
benzoic acid	CO_2	None	0	6	328.15	8.0	0.0695×10^{-3}	[2]
						11.0	0.3388×10^{-3}	
						13.0	0.6373×10^{-3}	
						17.0	2.4475×10^{-3}	
						20.0	3.6975×10^{-3}	
						23.0	4.2325×10^{-3}	
anthracene	CO_2	None	0	5	308.1	10.00	0.416×10^{-4}	[1]
						15.00	0.508×10^{-4}	
						20.00	0.696×10^{-4}	
						25.00	0.759×10^{-4}	
						30.00	0.783×10^{-4}	
anthracene	CO_2	None	0	5	318.1	10.00	0.205×10^{-4}	[1]
						15.00	0.539×10^{-4}	
						20.00	0.745×10^{-4}	
						25.00	0.851×10^{-4}	
						30.00	0.940×10^{-4}	
anthracene	CO_2	None	0	5	328.1	10.00	0.138×10^{-4}	[1]
						15.00	0.573×10^{-4}	
						20.00	0.807×10^{-4}	
						25.00	1.02×10^{-4}	
						30.00	1.13×10^{-4}	

[1] Li *et al*., 2003
[2] Jin *et al*., 2004
[3] Huang *et al*., 2004

Appendix C

Plots of Solubility versus Pressure – Modeling

The behavior of the solubilities using the estimated interaction parameters tabulated in Table 6 for the systems listed in Table 2 are presented in the following figures.
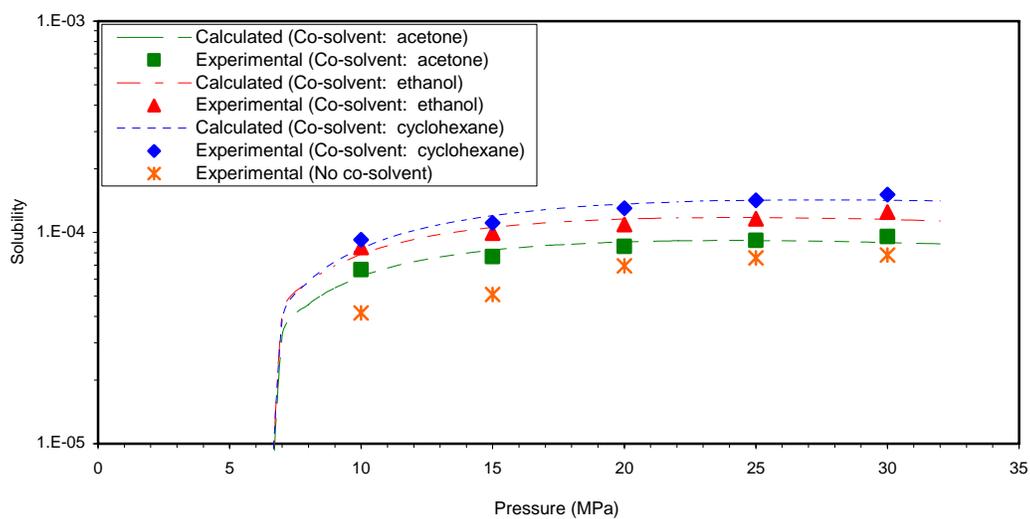
Figure 6. Comparison between calculated and experimental data for the system anthracene in CO_2 and three different cosolvents at 308.1 K. Cosolvent mole fraction: 4%.
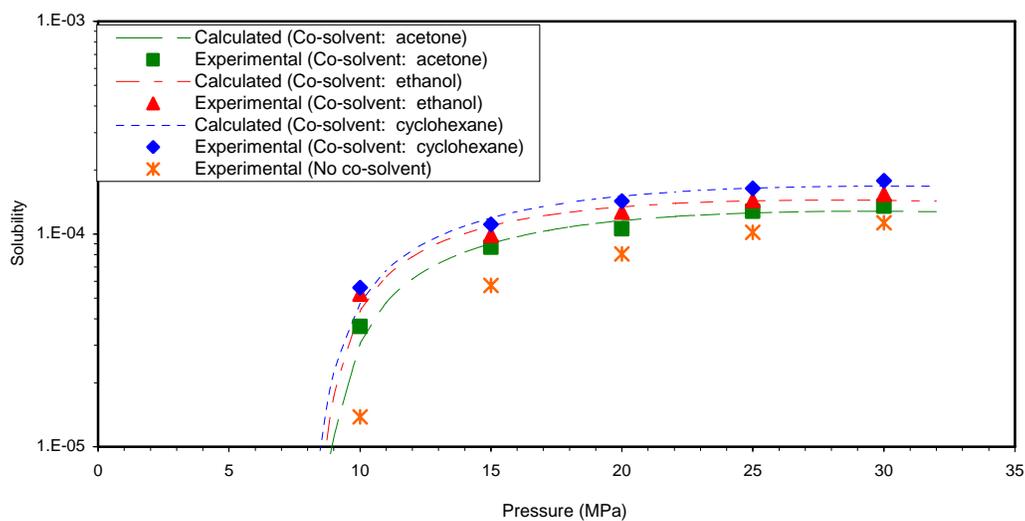
Figure 7. Comparison between calculated and experimental data for the system anthracene in CO_2 and three different cosolvent at 328.1 K. Cosolvent mole fraction: 4%.
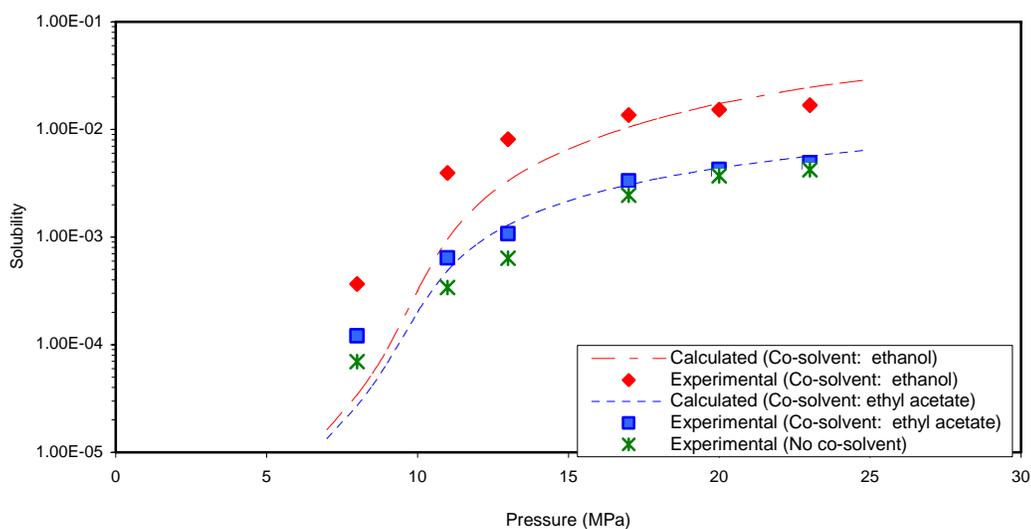
Figure 8. Comparison between calculated and experimental data for the system benzoic acid in CO_2 and two different cosolvents at 328.15 K. Cosolvent mole fraction: 2%.
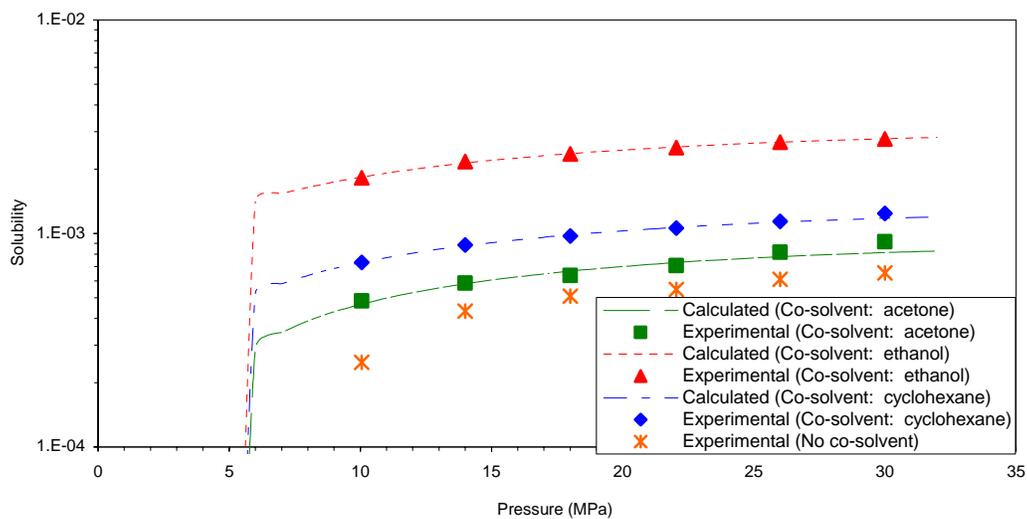
Figure 9. Comparison between calculated and experimental data for the system 2-naphthol in CO_2 and three different cosolvents at 308.1 K. Cosolvent mole fraction: 3.6%.
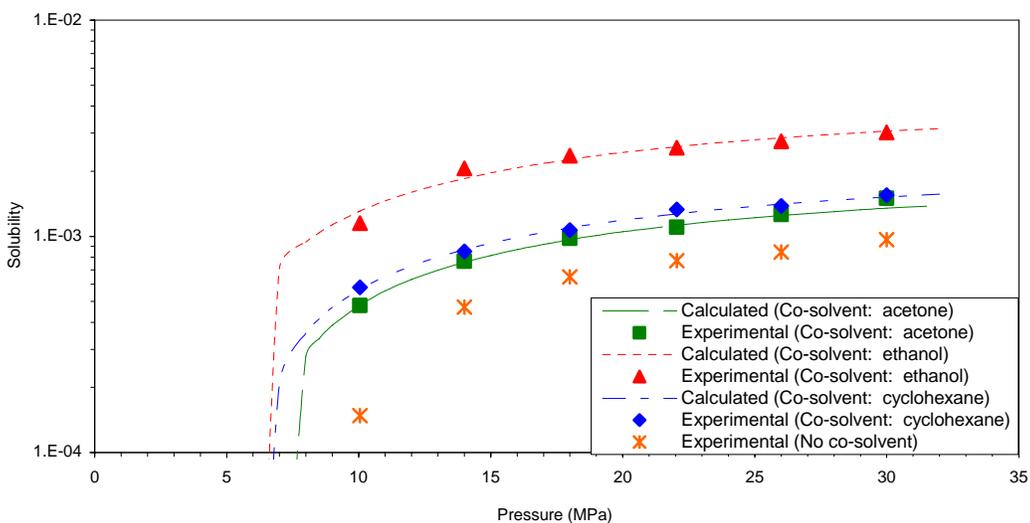
Figure 10. Comparison between calculated and experimental data for the system 2-naphthol in CO_2 and three different cosolvents at 318.1 K. Cosolvent mole fraction: 3.6%.
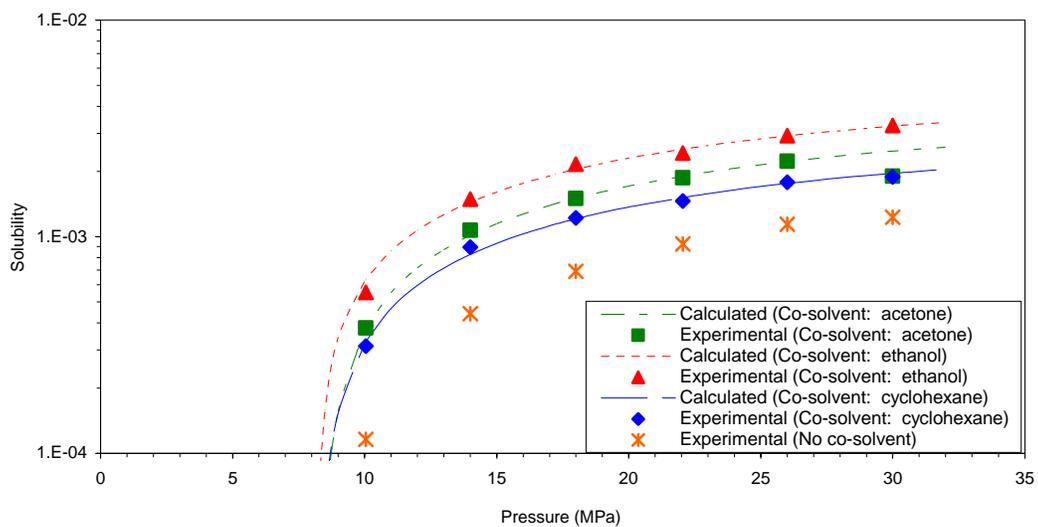
Figure 11. Comparison between calculated and experimental data for the system 2-naphthol in CO_2 and three different cosolvents at 328.1 K. Cosolvent mole fraction: 3.6%.
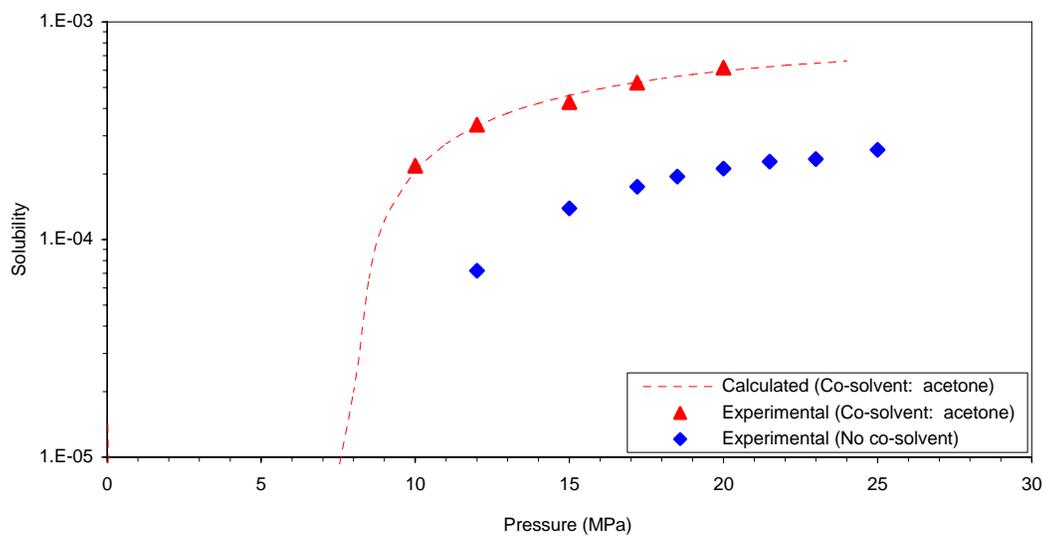
Figure 12. Comparison between calculated and experimental data for the system aspirin in CO_2 with 3% acetone at 318.15 K.
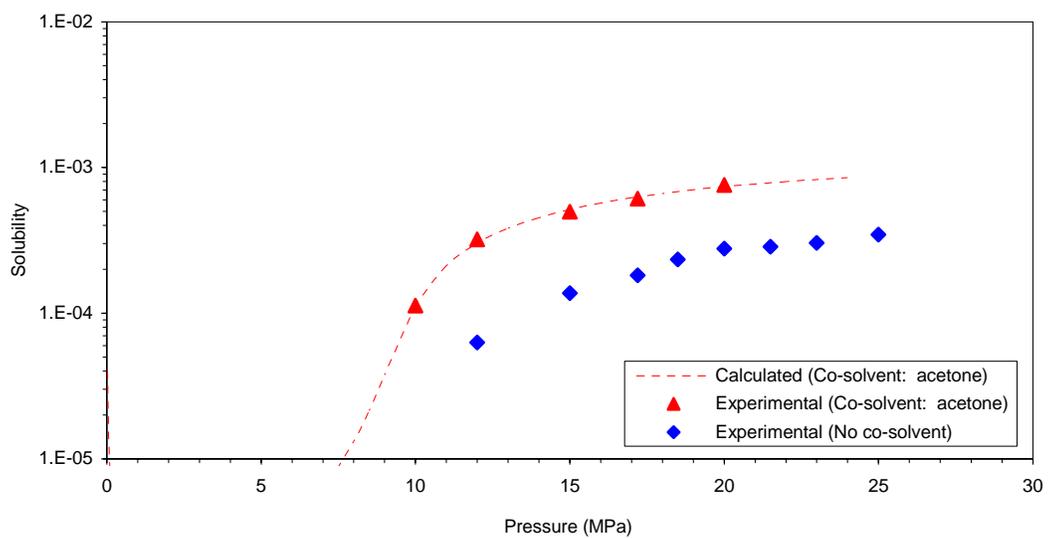
Figure 13. Comparison between calculated and experimental data for the system aspirin in CO_2 with 3% acetone at 328.15 K.

Appendix D

Plots of Solubility versus Cosolvent Concentration – Simulations
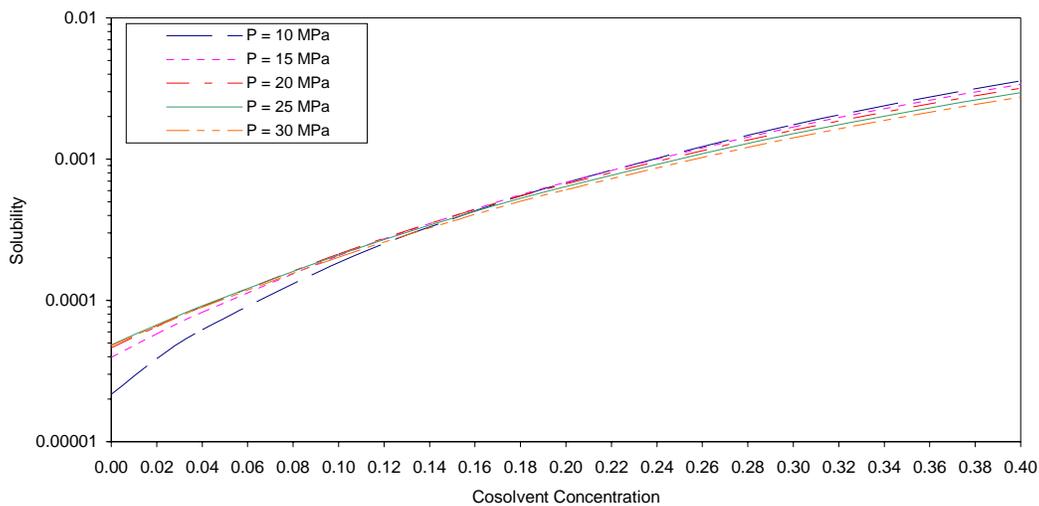
Figure 14. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and acetone as cosolvent at 308.1 K.
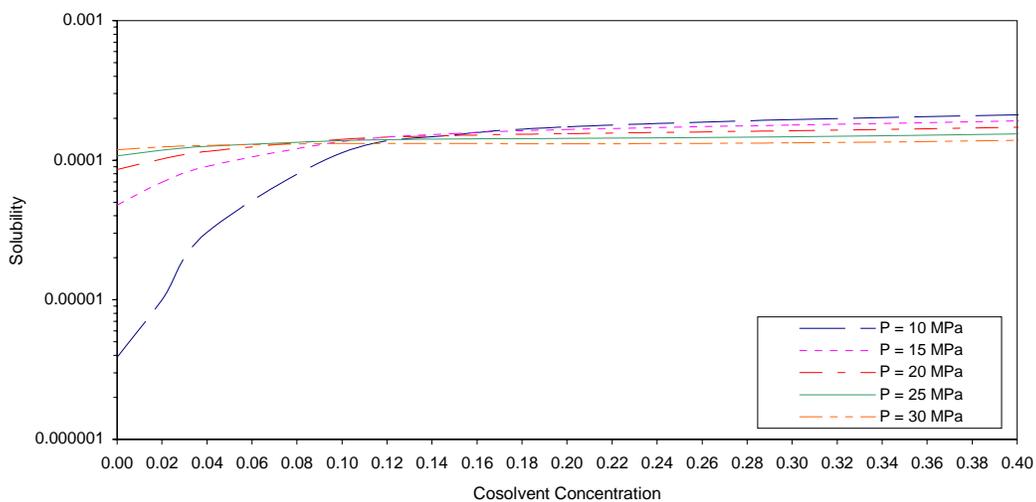

Figure 15. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and acetone as cosolvent at 328.1 K.
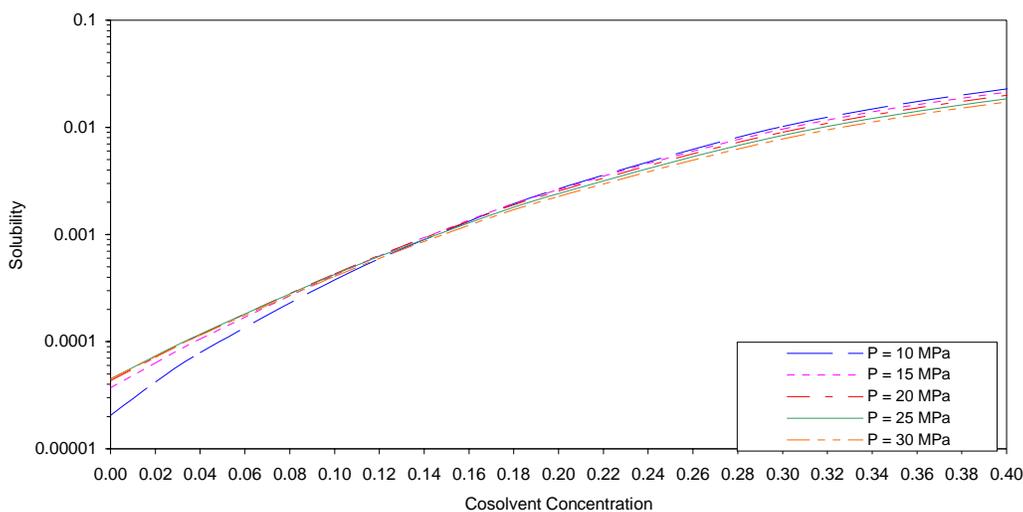
Figure 16. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and ethanol as cosolvent at 308.1 K.
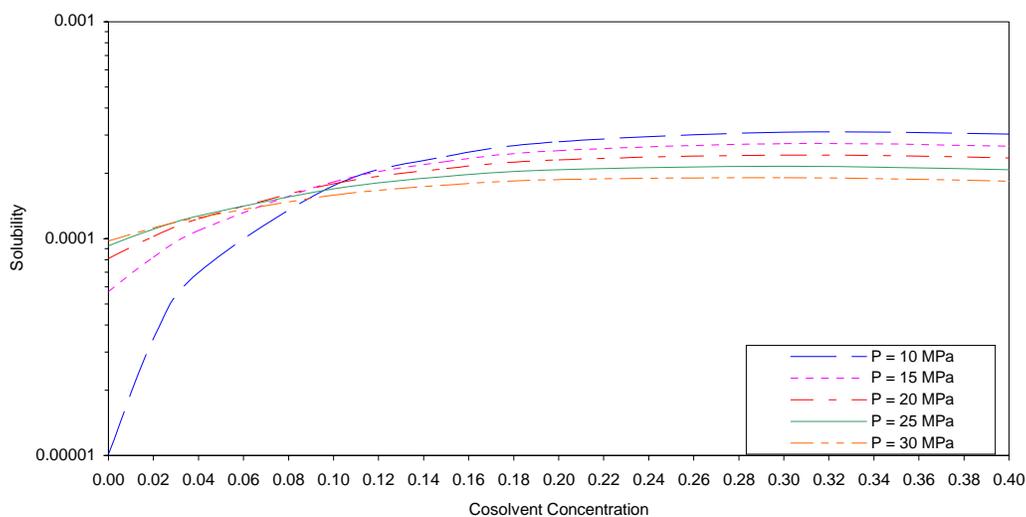
Figure 17. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and ethanol as cosolvent at 318.1 K.
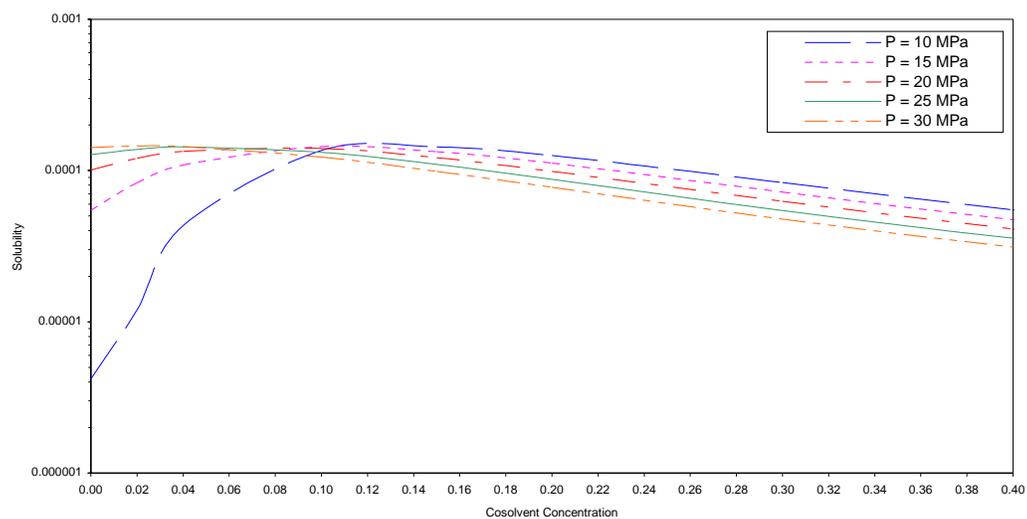
Figure 18. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and ethanol as cosolvent at 328.1 K.
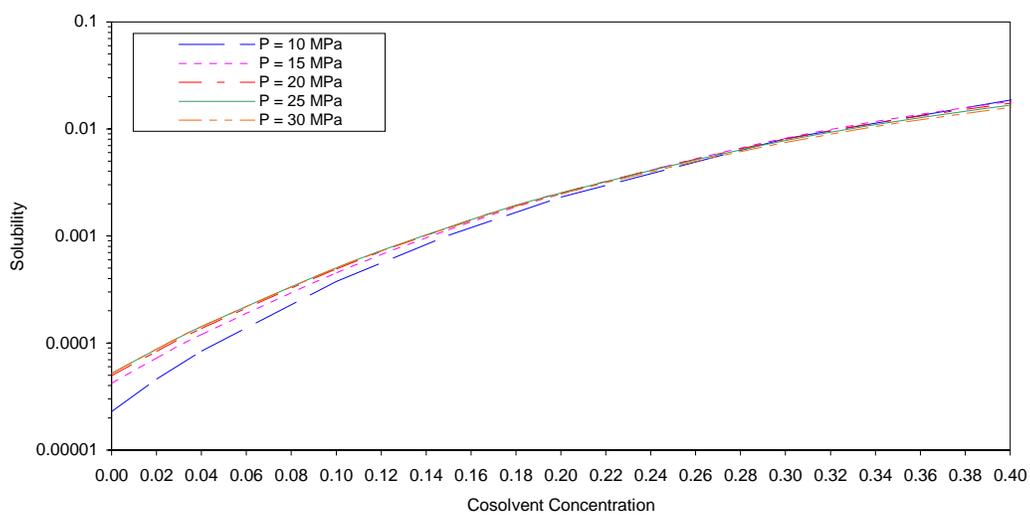
Figure 19. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and cyclohexane as cosolvent at 308.1 K.
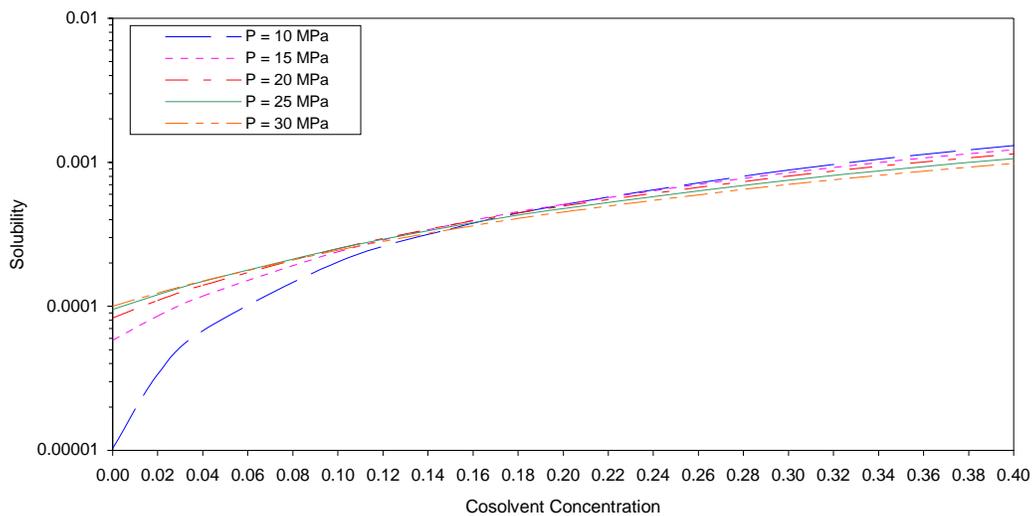
Figure 20. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and cyclohexane as cosolvent at 318.1 K.
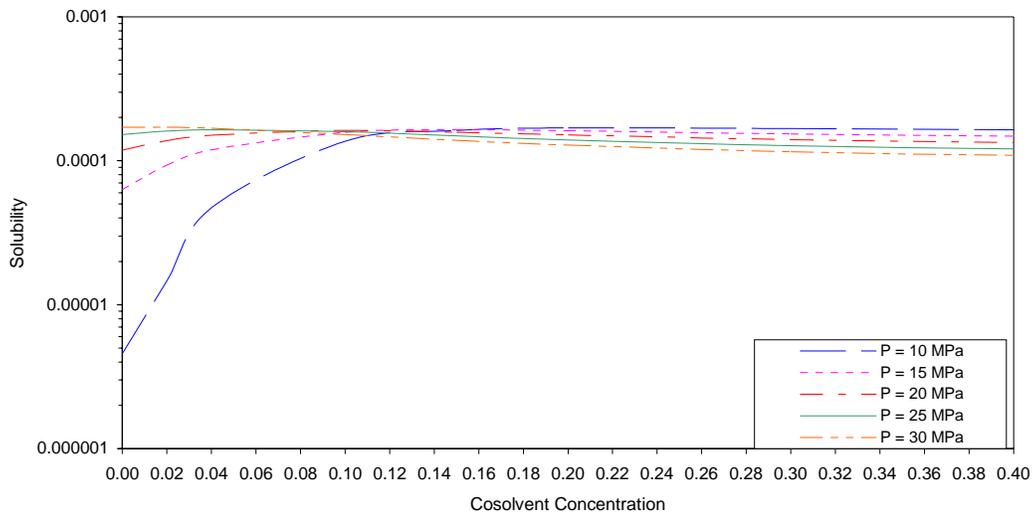

Figure 21. Effect of variation of cosolvent concentration on the solubility. System anthracene in supercritical CO_2 and cyclohexane as cosolvent at 328.1 K.
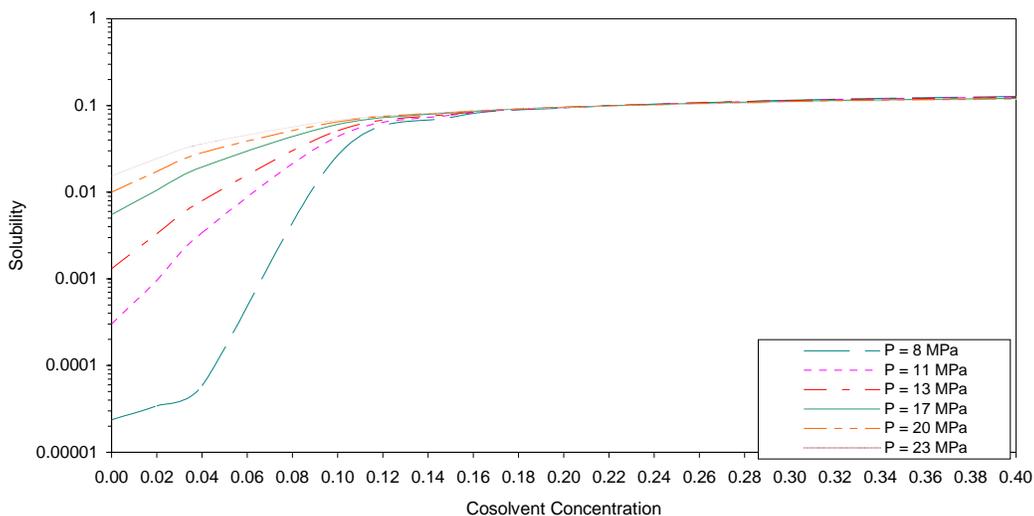
Figure 22. Effect of variation of cosolvent concentration on the solubility. System benzoic acid in supercritical CO_2 and ethanol as cosolvent at 328.15 K.
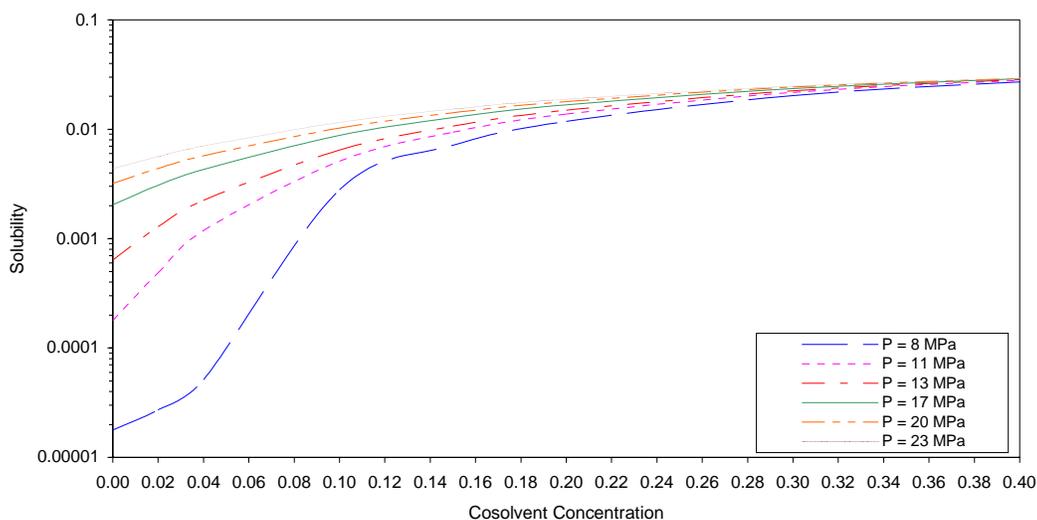
Figure 23. Effect of variation of cosolvent concentration on the solubility. System benzoic acid in supercritical CO_2 and ethyl acetate as cosolvent at 328.15 K.
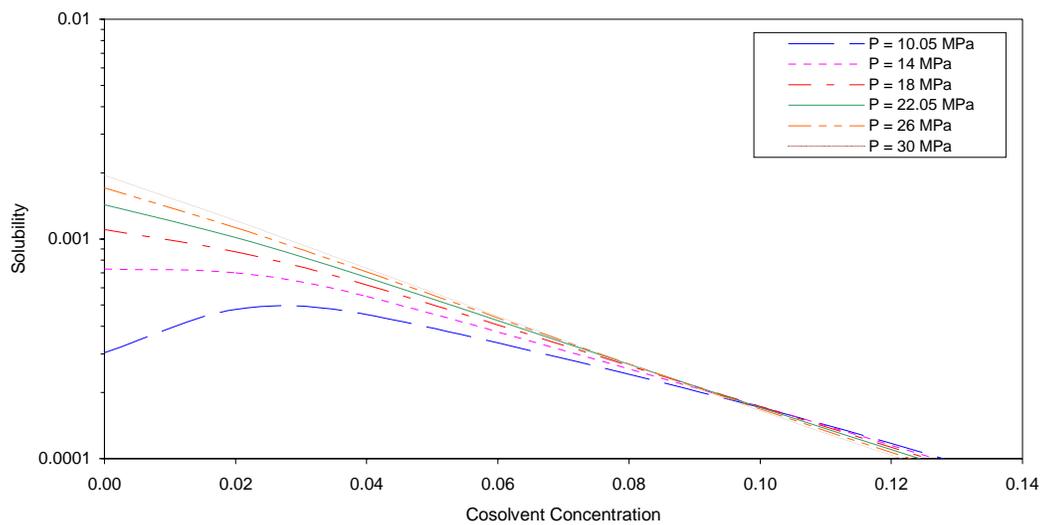
Figure 24. Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and acetone as cosolvent at 308.1 K.
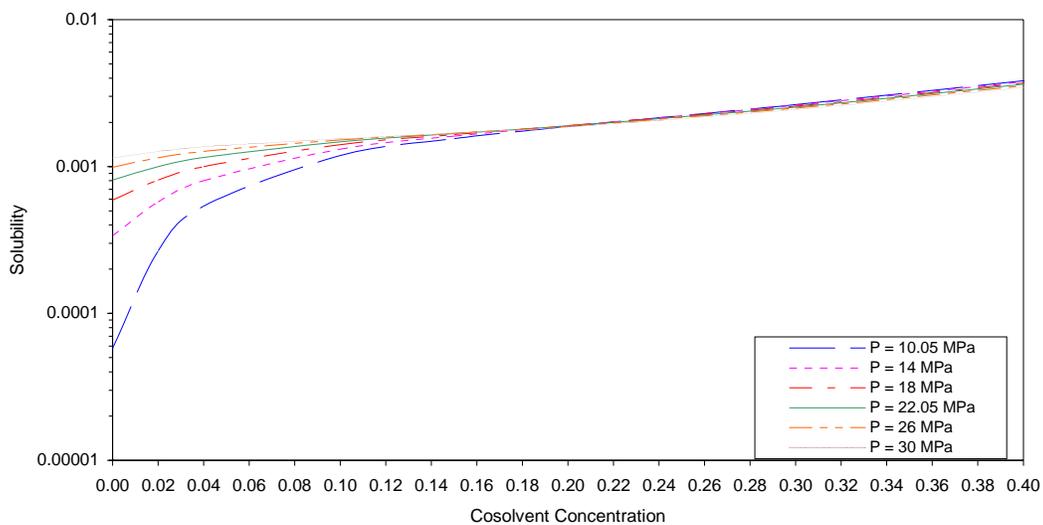
Figure 25. Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and acetone as cosolvent at 318.1 K.
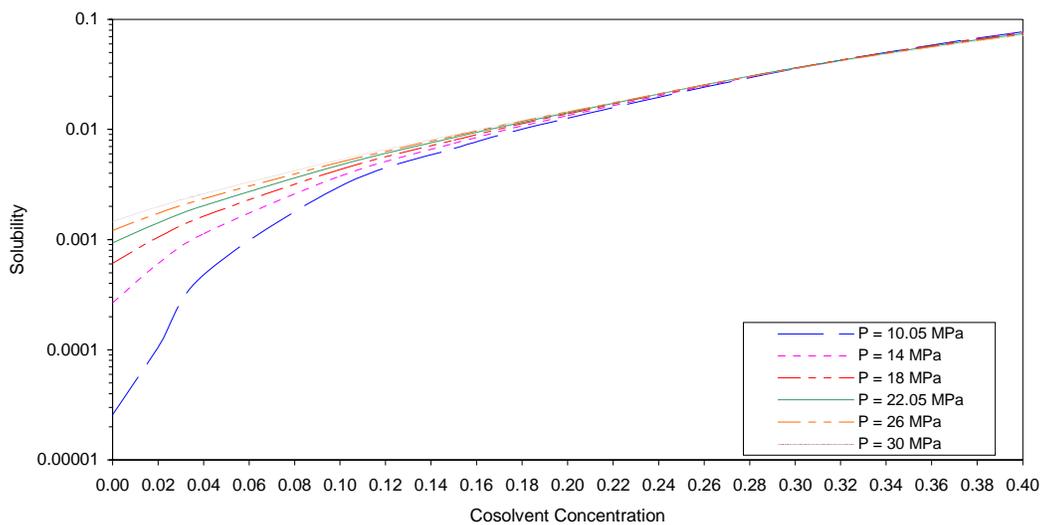
Figure 26. Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and acetone as cosolvent at 328.1 K.
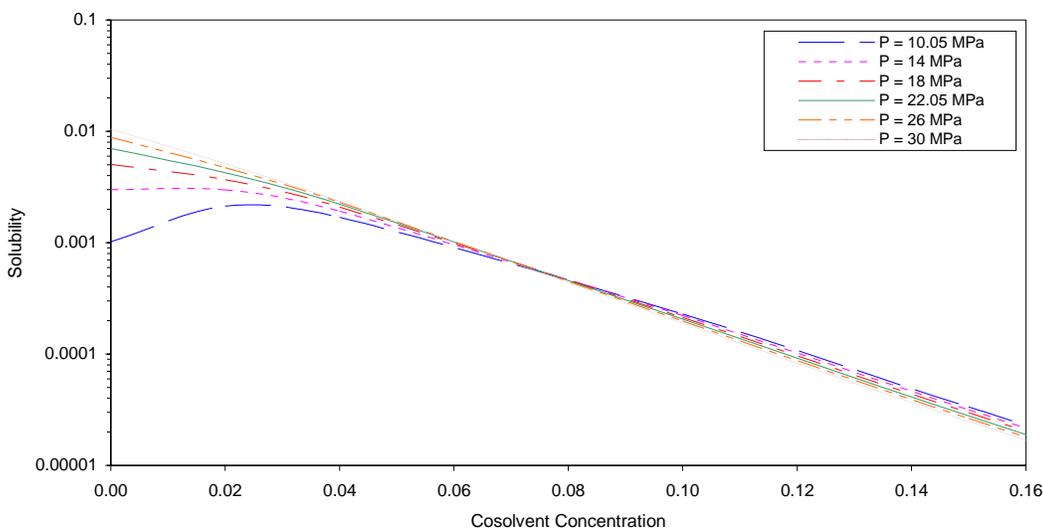
Figure 27. Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and ethanol as cosolvent at 308.1 K.
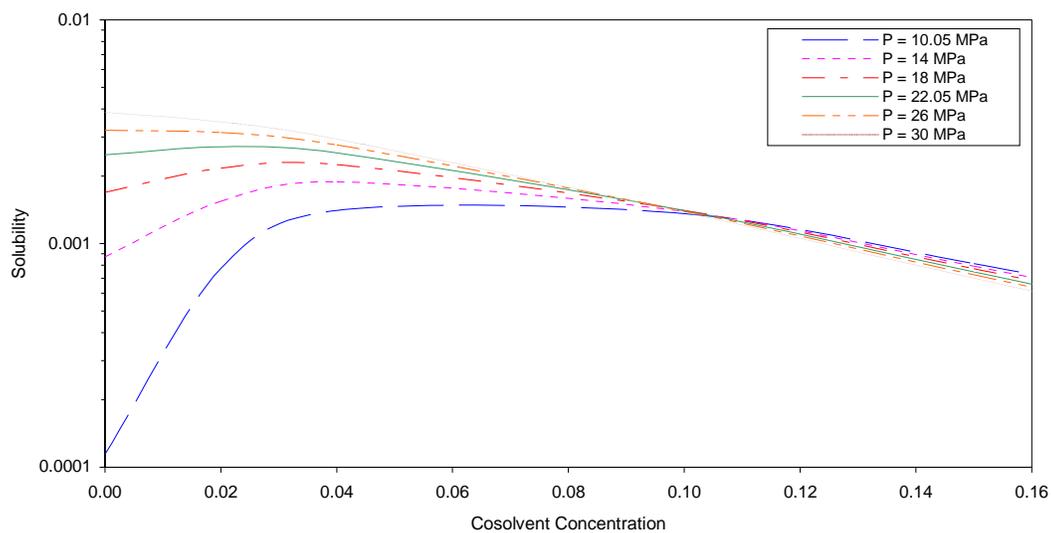
**Figure 28.** Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and ethanol as cosolvent at 318.1 K.
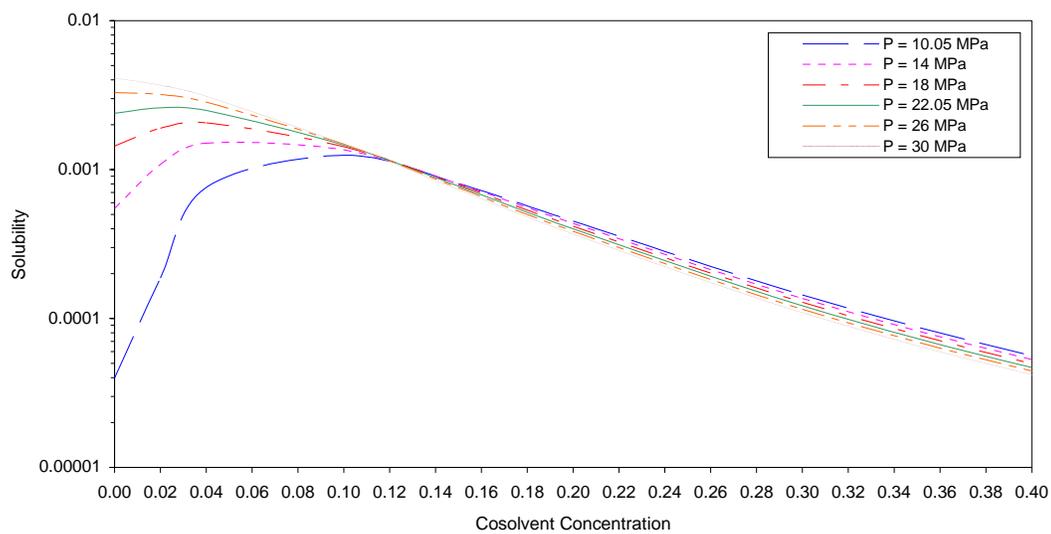
Figure 29. Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and ethanol as cosolvent at 328.1 K.
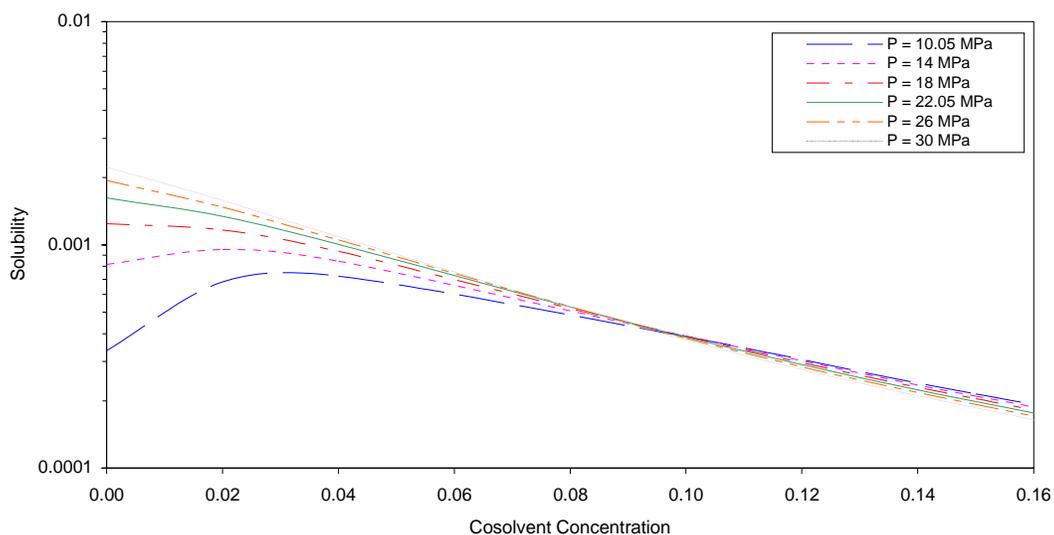
Figure 30. Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and cyclohexane as cosolvent at 308.1 K.
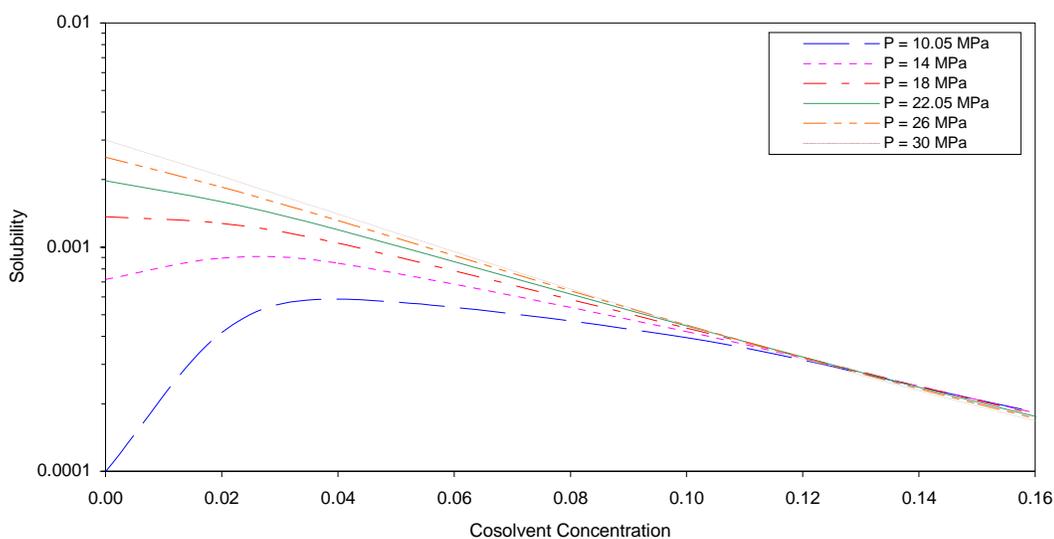
Figure 31. Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and cyclohexane as cosolvent at 318.1 K.
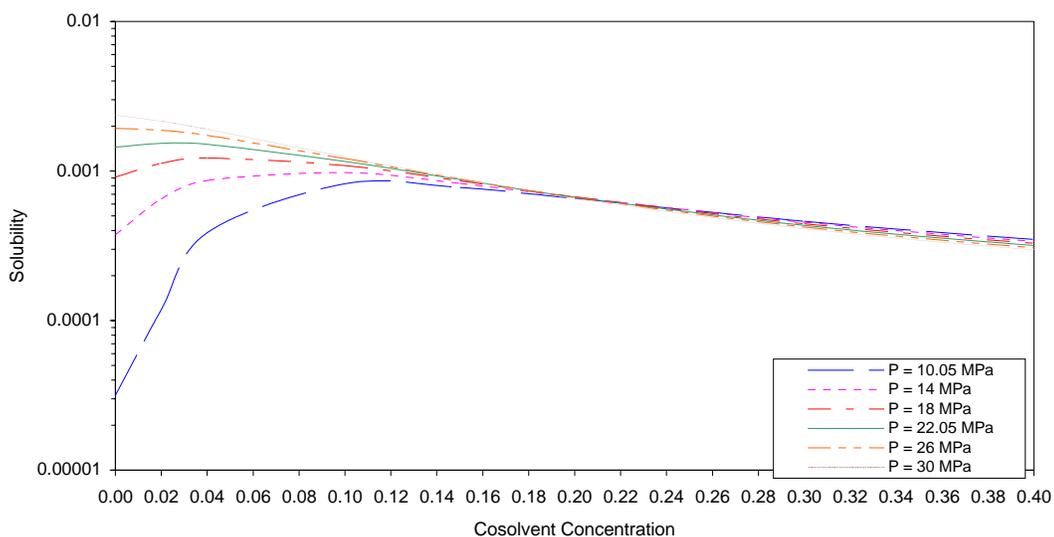
Figure 32. Effect of variation of cosolvent concentration on the solubility. System 2-naphthol in supercritical CO_2 and cyclohexane as cosolvent at 328.1 K.
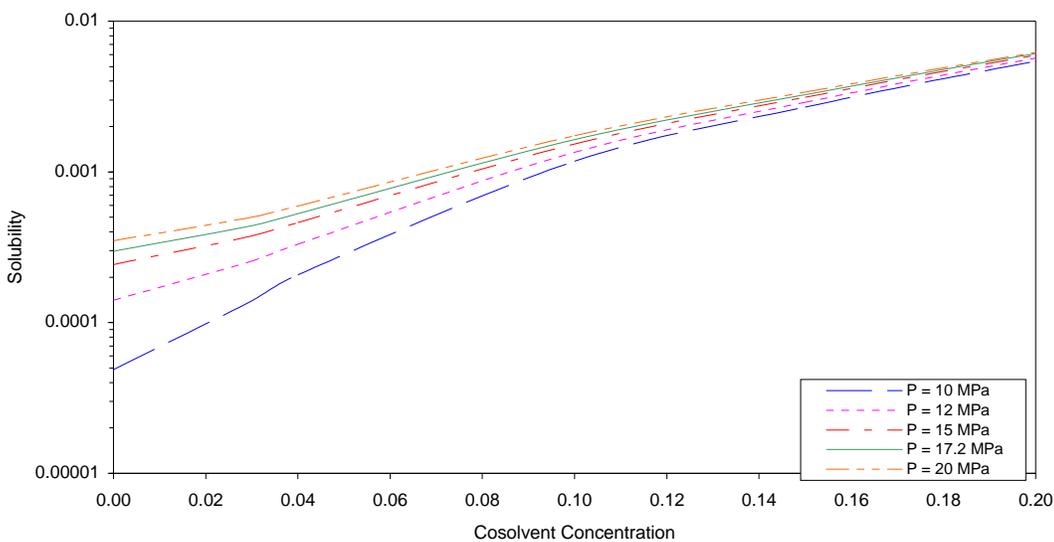

Figure 33. Effect of variation of cosolvent concentration on the solubility. System aspirin in supercritical CO_2 and acetone as cosolvent at 318.15 K.
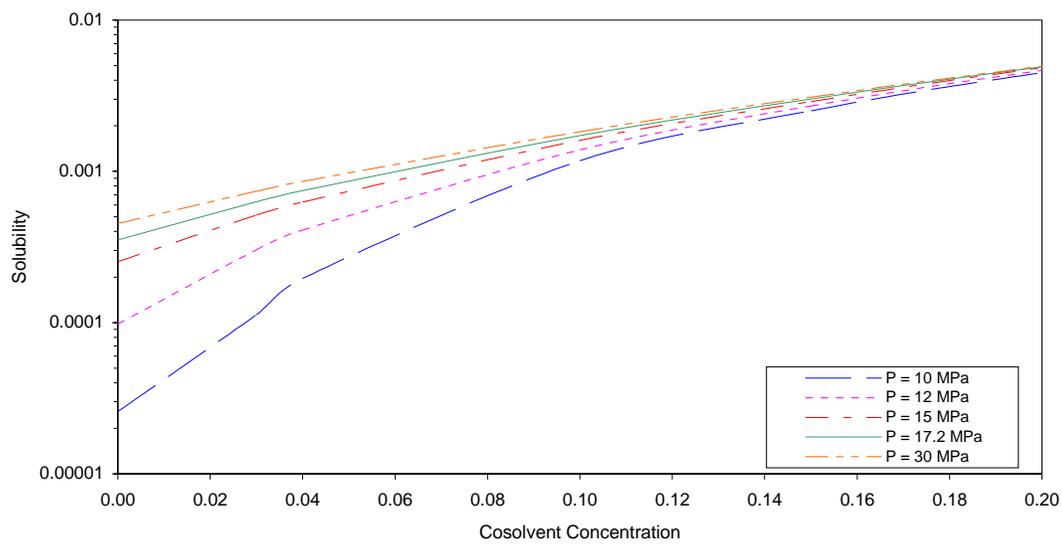
Figure 34. Effect of variation of cosolvent concentration on the solubility. System aspirin in supercritical CO_2 and acetone as cosolvent at 328.15 K.