A NEW MIXING RULE IN THE MODELING OF THE SOLUBILITY OF SOLIDS IN SUPERCRITICAL FLUIDS

by

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ABSTRACT

Currently, supercritical-fluid technology in the pharmaceutical and microelectronics industries is increasingly applied to solve difficult processing problems. The solubility of a solute in the supercritical fluid is the most important thermophysical property that needs to be determined and modeled as a first step to develop any supercritical fluids application. This research was undertaken to develop a mathematical model to compute the solubility of solids in supercritical fluids. As a result, a new combination rule is proposed along with a novel approach to obtain general correlations for its parameters. The new combination rule is a modification of the classical van der Waals mixing rules where the binary cohesive parameter a_{12} is correlated in terms of the reduced pressure. A database containing experimental solubility data for 126 isotherms was used in this study. Half of the isotherms were judiciously selected to develop the correlations in the new combination rule. The rest of the isotherms were then used to validate the results. Detailed error calculations were carried out for different thermodynamic models that included the Peng-Robinson and Patel-Teja equations of state and van der Waals, cubic, and Rao mixing rules. The conclusion, after comparing the calculated errors for various models, was that the best results were obtained for the Patel-Teja EoS and the new mixing rule proposed here. This work is a significant contribution in the field in two ways. First, it provides a specific correlation that gives excellent values of solubility. Second, it proposes a novel approach that can be extended to other mixing rules and may result in a fully predictive method.

RESUMEN

Actualmente, la tecnología de fluidos supercríticos en las industrias farmacéutica y de microelectrónica se aplica cada vez más para resolver problemas difíciles de proceso. La solubilidad de un soluto en un fluido supercrítico es la característica termofísica más importante que se debe determinar y modelar como un primer paso en el desarrollo de cualquier aplicación. Esta investigación se tomó para desarrollar un modelo matemático para el cálculo de la solubilidad de sólidos en fluidos supercríticos. Como resultado, se propone una nueva regla de combinación así como una forma novedosa de obtener sus parámetros. La nueva regla de combinación es un a modificación de las reglas de mezcla clásicas de van der Waals en donde el parámetro cohesivo binario a_{12} se correlaciona en términos de la presión reducida. En este estudio se usó una base de datos que contiene datos experimentales de solubilidad para 126 isotermas. La mitad de las isotermas se seleccionaron juiciosamente para desarrollar la correlación de la nueva regla de combinación. El resto de las isotermas se usaron para validar los resultados. Se hicieron cálculos detallados de los errores para diferentes modelos termodinámicos que incluyeron las ecuaciones de estado de Peng-Robinson y Patel-Teja y las reglas de mezcla de van der Waals, cúbica y de Rao. Luego de comparar los errores calculados para los diferentes modelos, se concluyó que los mejores resultados se obtuvieron para la ecuación de estado de Patel-Teja y la nueva regla de combinación aquí propuesta. Este trabajo constituye una contribución significativa en dos formas. Primero, se provee una correlación específica que da excelentes valores de solubilidad. Segundo, se propone un enfoque novedoso que puede ser extendido a otras reglas de mezcla que podrían dar como resultado un método completamente predictivo.

To God, my inseparable friend

To my family, the motor of my life

To my husband, by his love and comprehension

To my friends, for collaboration

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Roman Symbols

a   Equation of state constant that corrects for intermolecular attractive forces, $[N \cdot m^4/mol^2]$

A   Dimensionless equation of state parameter corresponding to a_m, [-]

b   Equation of state constant that corrects for the volume of gas molecules (covolume), $[m^3/mol]$

c   Equation of state constant

B   Dimensionless equation of state parameter corresponding to b_m, [-]

h_{12} Binary Interaction Parameter, [-]

k_1 Parameter of Stryjek and Vera

k_{12} Binary Interaction Parameter, [-]

P   Pressure, [Pa]

P_c Critical pressure, [Pa]

P_r Reduced pressure, [-]

R   Gas constant, [J/mol·K]

T   Temperature [K]

T_c Critical temperature [-]

T_r Reduced temperature, [-]

u   EOS parameter, [-]

V   Molar volume, $[m^3/mol]$

w   EoS parameter, [-]

Z   Compressibility factor, [-]

Greek Symbols

α   Dimensionless parameter temperature, [-]

η   Dimensionless parameter, [-]

θ   Dimensionless temperature, [-]

ξ   Dimensionless parameter of new mixing rule, [-]

ε   Dimensionless parameter, [-]

ω   Acentric factor, [-]

δ   Dimensionless parameter, [-]

Ω   Parameter of Equations of State

ψ   Parameter relation between the constants equation of state, *a*

Subscripts

i   Component *i* of the mixture

m   Mixture

Abbreviations

EoS   Equations of state

NMR   New mixing rule

PR   Peng-Robinson equation of state

PT   Patel-Teja equation of state

Rao   Mukhopadhyay-Rao mixing rule

SCF   Supercritical fluid

vdW   van der Waals mixing rule

1. INTRODUCTION

The term 'supercritical fluid' describes a fluid at conditions above its critical temperature and pressure i.e., above its critical point. Drawing from physical chemistry texts, the critical point is located at the end of the vapor-pressure curve Figure 1-1 shows a generalized vapor pressure curve and its end. The shaded region there in denotes a supercritical fluid space where many gases exhibit a special ability to dissolve materials (Krukonis 2000).
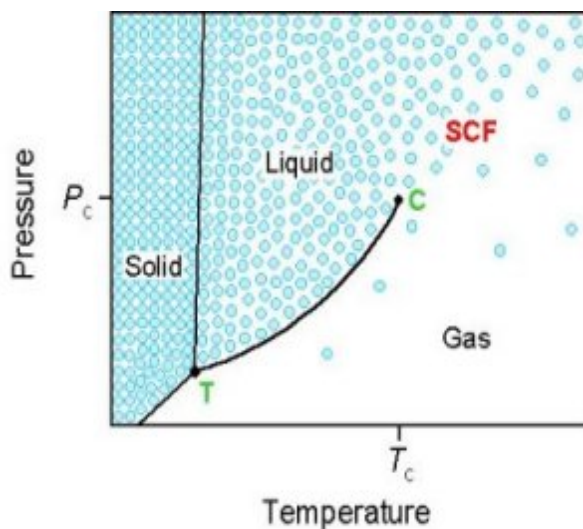
Figure 1-1. Phase Diagram of a Pure Component

Applications of supercritical fluids (SCF) in many fields have increased substantially, particularly in the pharmaceutical industry, for the solution of difficult processing problems. Supercritical fluids exhibit a pressure-tunable dissolving power, a liquid-like density (and thus a high solvent power), and gas-like transport properties, allowing easier extraction from dense botanical materials to be achieved. This unique

combination of properties is ideally suited for developing processes such as: extracting, purifying, and recrystallizing fine chemicals and pharmaceuticals products, as well as producing new product forms that cannot be obtained by traditional manufacturing processes.

1.1   Justification

Supercritical fluids nowadays have attracted great interest in the development of alternate processes to substitute traditional ones such as solvent extraction, distillation, and wiped film evaporation. Supercritical-fluid technology offers numerous advantages compared to conventional processes, such as high transfer rates, reduced number of unit operations, and lower operating costs (Chordia and Martínez, 2002). All this is enough motivation to pursue research in the field of supercritical fluids.

The peculiar characteristics of SCF have prompted supercritical fluids to be applied in the development of improved processes and products where: environmental-compliance pressures require a change in the process; the regulatory pressures require a change in product purity; increased product quality is required to create a new market position; and where none of these can be achieved by industry's more traditional industrial processes.

The solubility of a solute in a supercritical fluid is the most important thermophysical property to determine and model as a first step to develop any SCF application (García-González et al., 2002). Therefore, tools to help predict this important factor have to be developed. In Puerto Rico, there are a number of opportunities to develop processes for the pharmaceutical industry. Most of these involve solubilizing drugs and biomaterials in SCFs. Thus, predictive methods for solubilities of high-molecular-weight substances such as these are of crucial importance. Existing models are of limited applicability for various reasons, e.g., they have been developed for a particular system or they require adjustable parameters that cannot be generally predicted. This is the main justification to undertake a project aimed at finding a model as widely applicable as possible.

1.2 Goals and Methodology

1.2.1. Main Goal

This thesis was set forth to develop an improved mathematical model for the solubility of solids in supercritical fluids, i.e., a model better than those currently available. The model was to be based on modern versions of cubic equations of state and mixing rules. As research progressed, the idea of developing a new mixing rule came about. From then on, the main goal of the thesis was to work on a mixing rule.

1.2.2. Specific Goals

To achieve the main goal, the following sequential objectives are pursued:

1. Perform a thorough and comprehensive literature review of the equation of state (EoS) based models for the calculation of the solubility of solids in SCF. In this context, a model is a combination of an EoS and mixing rule.

2. Critically study the strengths and weaknesses of currently available models and select the best combination of EoS, and mixing rules to have a basis of comparison.

3. Update and expand the solubility database available from previous works within this research group.

4. Write a program in MATLAB that calculates the solubility of solids in SCF using any of the mathematical models selected in 2.

5. Develop a new mixing rule.

6. Expand the program written in 4 to use the new mixing rule with various EoS.

7. Compare all models studied.

8. Select the best model of all possible combinations of EoS and mixing rule, including the new mixing rule.

1.3   Literature Review

To predict the solubility of a solute in supercritical fluids, EoS models are widely used. Cubic EoS are the simplest equations capable of predicting and representing fluid phase equilibrium (Figueira et al., 2005). The first cubic EoS was proposed by van der Waals (1873). Although it has low accuracy, it has been the basis in the development of

a myriad of modifications, some of the best known being the Redlich-Kwong (1949), Soave (1972), and Peng Robinson (1976) equations.

Understanding the strengths and limitations of available models based on cubic equations of state (Chorng et al, 2002) is key to develop a sound mathematical model for the solubility of solids in SCFs. It is important to note that any model entails the selection of an equation of state and the mixing rules.

Frequently, investigators using van der Waals mixing rules are capable of representing vapor-liquid equilibria for non-polar or slightly polar systems. However, in the chemical industry, many mixtures contain strongly polar or associating components. Therefore, new mixing rules have arisen to help describe behavior of complex, highly non-ideal mixtures.

The Wong and Sandler (1979) model introduced a binary interaction parameter, to correct the assumption that the excess Helmholtz free energy at infinite pressure can be approximated by the excess Gibbs free energy a low pressure. Also, demonstrated that parameters in the activity coefficient models correlated at low temperatures can be used to extrapolate to higher temperatures (Chorng et al, 2002). Ghost and Taraphdar (1988) used Wong-Sandler mixing rules with the Peng-Robinson EoS modified by Stryjek and Vera to predict vapor-liquid equilibria of binary systems involving alcohols, esters,

ketones, amines, etc., but the working pressure range in all situations is quite low. The discrepancy observed may be attributed to the asymmetric nature of these systems.

Guha and Madras (2001) developed a new model for the solubilities of solid solutes in supercritical carbon dioxide that combines the cubic Patel-Teja EoS with the Wong-Sandler mixing rules. The versatility of this model is indicated by the ability of the model to predict successfully the solubilities of both polar and non-polar mixtures, and provides a better correlation than the conventional model that use Peng-Robinson with simple or Wong-Sandler mixing rules.

In recent years, investigators have proposed or tested different models to calculate the solubility of solutes in supercritical fluids. For example, Caballero et al. (1992) calculated binary interaction parameters for the description of solid-supercritical fluid equilibrium using solubility data. The equations of state chosen were Redlich-Kwong, Soave, and Peng-Robinson, whereas the mixing rules used were quadratic (van der Waals) and cubic. When only one interaction parameter was used the three EoSs tested gave similar results in terms of average errors. The differences found for individual systems are compared, in terms to of the ability of the EoS to predict molecular interactions in these systems. For the Peng-Robinson, the quadratic and cubic mixing rules showed no substantial difference when the average errors are compared, although the error for the cubic mixing rule is systematically lower than for the quadratic one.

Finally, a marked reduction in the error was observed when the second binary interaction parameter was included in the analysis.

Estévez et al. (1994) applied a simplified method; the infinite dilution fugacity coefficient of the solute was computed using the pure solvent compressibility factor. The proposed model proved to be an easy way to correlate the solubility of high-molecular-weight solids, because it does not require the values of critical temperature or critical pressure of the solute. The Redlich-Kwong EoS is simpler to use and produced similar accuracy in the predictions as the Peng Robinson EoS; therefore, they recommended it for faster, even manual, calculations.

Summarizing, for the prediction and calculation of the solubility of solids in supercritical fluids, classical cubic EoSs have been used (Ashour et al. 2000, Soave 2000, and Coutsikos et al. 2003) and modern (Ghosh and Taraphdar 1988), with different mixing rules (Caballero and Estévez, 1991, and Huang et al. 2001).

The review presented here is not meant to be comprehensive but illustrates the type of approaches found in the literature. Other references not mentioned above, but certainly relevant in the field, are listed in Table 1-1; these are recent modeling references of importance for the calculation of solubility of supercritical fluids.

Table 1-1. Recent Modeling References

Reference	Correlation	Model	
		EOS	**Mixing Rules**
Muller et al.,1989		PR Residual Properties	Mixing general and combinations
Valderrama et al., 2003	Regular Solution Model	vdW SRK PR Patel-Teja-Valderrama	Classical Mixing Rules
Valderrama et al., 2002		SRK PR Generalized three-constant EOS	Panagiotopoulos-Reid and Adachi-Sugie
Panduranga et al., 1992		PR SRK vdW	vdW
Garnier et al., 1999	–	PR-R, PR-C	vdW
Boukouvalas et al., 2001	Models: LCVM and PHCT		

2. THEORETICAL BACKGROUND

2.1 Cubic Equations of State

Cubic EoS can be expressed in a general form of five parameters as (Abbott, 1979):

$$P = \frac{RT}{V-b} - \frac{\Theta(V-\eta)}{(V-b)(V^2+\delta V+\varepsilon)} \tag{2-1}$$

where, depending on the equation, the parameters Θ, b, η, δ, and ε may be constants, including zero, or may vary with temperature (T) and/or composition (y_i) in the equation of state. Most recent EoS have used $\Theta(T) = a\alpha(T)$, where $\alpha(T_c) = 1$. The composition dependence is accounted for by the mixing rules.

The parameters a and b, for most equations of state, are given by:

$$a = \frac{\Omega_a R^2 T_c^2}{P_c} \tag{2-2}$$

$$b = \frac{\Omega_b R T_c}{P_c} \tag{2-3}$$

Table 2-1 shows relations and values for parameters in several common cubic EoS. Parameter b, in all cases listed, is a positive constant and $\eta = b$. The temperature dependence is included in the parameter $\alpha(T_r)$ where T_r is reduced temperature, thought b, c, d, etc. may depend on temperature.

Table 2-1. Parameters for Cubic EoS given by Equation 2-1

EoS	δ	ε	Θ
van der Waals (1890)	0	0	a
Redlich and Kwong (1949)	0	0	$\dfrac{a}{T_r^{0.50}}$
Soave (1972)	b	0	$a\alpha(T_r,\omega)$
Peng and Robinson (1976)	$2b$	$-b^2$	$a\alpha(T_r,\omega)$
Patel and Teja (1982)	$b+c$	$-bc$	$a\alpha(T_r,\omega)$
Stryjek and Vera (1986)	$2b$	$-b^2$	$a\alpha(T_r,\omega)$

Table 2-2 shows the expressions for $\alpha(T_r)$ in common cubic EoS. Therefore, all parameters are known for these cubic EoS.

Table 2-2. Expressions for $\alpha(T_r)$ in Common Cubic EoS for $T_r = T/T_c \leq 1$

EoS	$\alpha(T_r)$
van der Waals (1890)	1
Redlich and Kwong (1949)	$\dfrac{1}{T_r^{1/2}}$
Soave (1972)	$\left[1+\left(0.48+1.574\omega-0.176\omega^2\right)\left(1-T_r^{1/2}\right)\right]^2$
Peng and Robinson (1976)	$\left[1+\left(0.37464+1.54226\omega-0.2699\omega^2\right)\left(1-T_r^{1/2}\right)\right]^2$
Patel and Teja (1982)	$\left[1+F\left(1-T_r^{1/2}\right)\right]^2$ $F=\left[1+\left(0.452413+1.38092\omega-0.295937\omega^2\right)\left(1-T_r^{1/2}\right)\right]^2$
Stryjek and Vera (1986)	$\left[1+\left(0.378893+1.4897153\omega-0.17131848\omega^2+0.0196554\omega^3\right)\left(1-T_r^{1/2}\right)\right]^2$ $+k_1\left(1-T_r\right)\left(0.7-T_r\right)$

Equation (2-1) may be expressed in terms of Z as follows:

$$Z = \frac{V}{V-b} - \frac{(\Theta/RT)V(V-\eta)}{(V-b)(V^2+\delta V+\varepsilon)} \tag{2-4}$$

The polynomial form of equation 2-4 is:

$$Z^3 + (\delta^* - B - 1)Z^2 + \left[\Theta^* + \varepsilon^* - \delta^*(B+1)Z\right] - \left[\varepsilon^*(B+1) + \Theta^*\eta^*\right] = 0 \tag{2-5}$$

where the dimensionless parameters are defined as:

$$B \equiv \frac{bP}{RT} \tag{2-6}$$

$$\delta^* \equiv \frac{\delta P}{RT} \tag{2-7}$$

$$\Theta^* \equiv \frac{\Theta P}{(RT)^2} \tag{2-8}$$

$$\varepsilon^* \equiv \frac{\varepsilon P}{RT} \tag{2-9}$$

$$\eta^* \equiv \frac{\eta P}{RT} \tag{2-10}$$

The solution of equation (2-5) requires finding the roots of a cubic polynomial. An analytical solution for that is provided in Appendix A.

2.2   Mixing Rules

Equation of state are applied to pure component and mixtures; the difficulty in the case of mixtures is to find rules to obtain mixtures parameters that now depend on the

mixture composition. For this reason, modern mixing rules are formulated in a manner to yield the least error when the predictions of the equations of state are compared with experimental data. To formulate the mixture EoS parameters, these are expressed in terms of explicit, equations that depend on the composition that use pure component parameters and mole fraction.

Cubic EoS includes the dispersion forces between the components of a mixture and combination rules give the EoS composition dependence. The inclusion of adjustable parameters or correction factors in the Cubic EoS account for specific chemical interactions such as hydrogen bonding and acid-base type interactions and complexities in the molecular interactions fields a different size, structure, polarity and energies of the components due to the great differences in their critical temperature. These correction factors are known as binary interaction parameter, and these are a measure of the deviations from the behavior expected in non-polar symmetric systems.

Conventional van der Waals mixing rules express the mixture cohesive energy parameter, a_m, and the mixture cohesive energy parameter b_m, of the EoS in terms of a quadratic composition dependence. They may use one or two binary interaction parameters: k_{ij} measures the deviation from geometric intermolecular interactions assumed for the unlike cohesive energy parameter a_{ij}, while the h_{ij} measures the deviation from arithmetic intermolecular interactions repulsions assumed for the unlike repulsive energy parameter b_{ij}. These binary interaction parameters can be positive or negative. Physically, a nonzero value of the k_{ij} indicates the presence in the mixture of specific

chemical interaction such as hydrogen bonding. For h_{ij}, it is difficult to establish a physical meaning because there are not sufficient data on this parameter to establish a trend on its values; in many cases, a value of zero is used in the cubic EoS to predict solubilities because it is not necessary to use both binary interaction parameters to predict phase behavior.

The van der Waals mixing rules may be used to calculate the mixture parameters a and b of any EoS. For a binary mixture:

$$a_m = a_{11}y_1^2 + a_{22}y_2^2 + 2a_{12}y_1y_2 \qquad \textbf{(2-11)}$$

and

$$b_m = b_{11}y_1^2 + b_{22}y_2^2 + 2b_{12}y_1y_2 \qquad \textbf{(2-12)}$$

where y_i represent the mole fraction of component i, and a_{ii} and b_{ii}, correspond to pure components and are given by equation (2-2) and (2-3). The following equations, often called combination rules, are normally used to calculate a_{12} and b_{12}:

$$a_{12} = \sqrt{a_{11}a_{22}}\left(1-k_{12}\right) \qquad \textbf{(2-13)}$$

and

$$b_{12} = \left(\frac{b_{11}+b_{22}}{2}\right)\left(1-h_{12}\right) \qquad \textbf{(2-14)}$$

where k_{12} and h_{12} represent the binary interaction parameters. When h_{12} is zero, equation (2-14) simplifies to:

$$b_m = \sum_{i=1}^{2} y_i b_{ii} \qquad \textbf{(2-15)}$$

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2.3   Solubility of Solids in Supercritical Fluids

The solubility of solids in supercritical fluids is given by:

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

(2-16)

where the fugacity coefficient, φ_i, is given by:

$$\ln \varphi_i = \frac{1}{RT}\int_V^\infty\left[\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} - \frac{RT}{V}\right]dV - \ln Z$$

(2-17)

Solving the integral in the equation (2-17), yields:

$$\ln \varphi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) + AQ_i$$

(2-18)

The expression for Q_i depends on the discriminant Δ, defined by:

$$\Delta = u^2 - 4w$$

(2-19)

where the parameters u and w depend on the cubic equations of state. Table 2-3, shows the values of u and w for some cubic EoS.

Table 2-3. Values of u and w for Common Cubic EoS

Equation	u	w
van der Waals	0	0
Redlich and Kwong	1	0
Peng and Robinson	2	−1
Patel and Teja	$\dfrac{(b+c)}{b}$	$\dfrac{-c}{b}$

For $\Delta \neq 0$:

$$Q_i = \frac{1}{g\Delta}\left[\frac{b_i}{b}Z\Delta + \left(s_i u - 2r_i w\right)B - \left(r_i u - 2s_i\right)Z\right] + \frac{L}{\Delta}\left[\left(\frac{a_i}{a} + 1\right)\Delta - \left(r_i u - 2s_i\right)\right] \quad \textbf{(2-20)}$$

where

$$g(T, V, N_1, ..., N_n) = V^2 + u(Nb)V + w(Nb)^2 \quad \textbf{(2-21)}$$

When $\Delta = 0$ **:**

$$Q_i = L\left[\frac{a_i}{a} + \left(\frac{b_i}{b}Z + \frac{r_i}{2}B\right)L + 1\right] \quad \textbf{(2-22)}$$

where

$$r_i = \left(u_i - u\right) + u\frac{b_i}{b} \quad \textbf{(2-23)}$$

and

$$s_i = \left(w_i - w\right) + 2w\frac{b_i}{b} \quad \textbf{(2-24)}$$

The parameter L in equations (2-20) and (2-21) also depends on the value of Δ.

When $\Delta > 0$:

$$L = \frac{1}{B\sqrt{\Delta}}\ln\left[\frac{2Z + B\left(u - \sqrt{\Delta}\right)}{2Z + B\left(u + \sqrt{\Delta}\right)}\right] \quad \textbf{(2-25)}$$

If $\Delta = 0$ **:**

$$L = \frac{2}{2Z + uB} \quad \textbf{(2-26)}$$

When $\Delta < 0$ **:**

$$L = \frac{2}{B\sqrt{-\Delta}} \tan^{-1} \left[\frac{2Z + uB}{B\sqrt{-\Delta}} + \frac{\pi}{2} \right]$$ **(2-27)**

The underlined variables with subscript i in this section represent composition derivates defined as partial molar properties; they are tabulated for a number of EoS elsewhere (Müller et al., 1989).

2.4 Prediction of the Solubility of Solids in Supercritical Fluids

The solubility of solids in supercritical fluids can be predicted from a thermodynamic model using an optimum binary interaction parameter should be found by minimizing an objective function (*OF*). The objective function is a measure of the deviations between predicted and experimental values; in this case, the root-mean-square of the absolute deviations has been adopted as *OF*:

$$OF = \sqrt{\frac{\sum_{i=1}^{N_p} \left(y_{i,cal} - y_{i,\exp} \right)^2}{N_p}}$$ **(2-28)**

To appreciate the quality of the predictions, the percent average error (*% AVERR*) is used, which is given by:

$$AVERR = 100 \frac{\sqrt{\dfrac{\sum_{i=1}^{N_p} \left(y_{i,cal} - y_{i,\exp} \right)^2}{N_p}}}{\overline{y_{\exp}}} = 100 \frac{OF}{\overline{y_{\exp}}}$$ **(2-29)**

$$AVERR = 100 \frac{N_p}{\sum_{i=1}^{N_p} y_{i,\exp}} OF$$ **(2-30)**

3. THERMODYNAMIC MODELS

Different thermodynamic models have been used to calculate the solubility of solid in a supercritical fluid. These models are conformed by an equation of state and mixing rules and are compared by using experimental data of different systems to determine which of them provides the best fit. A classic thermodynamic model, for example, is the Peng Robinson EoS and van der Waals mixing rules.

To assess the relative quality of the different thermodynamic models, a database composed by five solvents and twelve solutes was used which encompasses many systems at different temperatures and pressures. Table 4-1 and 4-2 show the values of the physical properties of the supercritical solvents and the solutes.

Table 3-1 Properties of the Supercritical Solvents

Solvent	M [g/mol]	P_c [MPa]	T_c [K]	ω
Chlorotrifluoromethane	104.459	3.92	301.95	0.108
Carbon dioxide	44.010	7.38	304.25	0.225
Ethane	30.070	4.88	305.35	0.098
Ethylene	28.054	5.03	282.40	0.089
Fluoroform	70.013	4.88	299.15	0.275

Table 3-2. Physical Properties of the Solutes

Solute	M [g/mol]	P_c [MPa]	T_c [K]	ω	A	B [K]	$10^3 \times V^{sol}$ [m³/mol]
Benzoic Acid	122.124	4.50	752.00	0.62000	14.408	4618.1	0.0965
Naphthalene	128.174	4.05	748.15	0.3020	13.583	3733.9	0.1103
2,3-dimethynaphtalene	156.23	3.22	785.00	0.4240	14.0646	4302.5	0.1547
2,6-dimethynaphtalene	156.23	3.22	777.00	0.4201	14.4286	4419.5	0.1547
1,4-naphthoquinone	158.16	4.12	792.15	0.5760	14.735	4739.4	0.1112
Hexamethylbenzene	162.276	2.38	752.00	0.4980	13.1336	3855.0	0.1526
Fluorene	166.23	2.99	821.00	0.4070	14.2046	4561.8	0.1393
Anthracene	178.234	3.12	869.30	0.3531	12.147	4397.6	0.1426
Phenanthrene	178.24	3.17	882.55	0.3299	14.631	4873.4	0.1512
Acridine	179.22	3.19	883.15	0.4980	13.721	4740.1	0.1783
Hexachloroethane	236.74	3.45	714.60	0.1630	10.6322	2600.94	0.1132
Triphenylmethane	244.34	2.24	863.00	0.5760	14.7858	5228.0	0.2409

The thermodynamic models analyzed were conformed in the following way: Peng-Robinson with Mukhopadhyay and Rao, van der Waals and cubic mixing rule and Patel-Teja with van der Waals mixing rule.

3.1   Peng-Robinson Model with Mukhopadhyay-Rao Mixing Rules

This model is composed of the Peng-Robinson EoS and a recent mixing rule proposed for Mukhopadhyay and Rao (1999); they increased the number of binary adjustable parameters but that did not improve the accuracy of the calculations. This mixing rule suggests a co-volume-dependent rule for parameter *a* with only one interaction parameter. They assumed that, in a dilute supercritical mixture, the molecules have large size differences; the probability of a molecule interacting with another in its vicinity depends on what fraction of the surface of the other molecule it can see rather than its relative number or mole fraction. Their repulsive forces become increasingly important in quantifying the energy of interaction for large size molecules. Therefore, an

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inverse co-volume dependency was introduced for the attraction energy parameter to account for the asymmetry and non-randomness. The Mukhopadhyay-Rao mixing rule is given by:

$$a_m = \sum_i^{n_c} \sum_i^{n_c} y_i y_j a_{ij} \left(\frac{b}{b_{ij}} \right)^{m_{ij}}$$

(3-1)

$$b_m = \sum_i^{n_c} y_i b_{ij}$$

(3-2)

where

$$a_{ij} = \sqrt{a_i a_j}$$

(3-3)

$$b_{ij} = \sqrt{b_i b_j}$$

(3-4)

The choice of $m_{ii} = m_{jj}$ reduces the sensitivity of the parameter m_{ij} while restricting the number of parameters to only one.

3.2   Peng-Robinson Model with van der Waals Mixing Rules

This model is conformed by Peng-Robinson and the van der Waals mixing rules; both have been described in Chapter 2. It the most commonly used model to calculate of the solubility of solids in supercritical fluids.

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3.3 Peng-Robinson Model with Cubic Mixing Rules

In this model, the Peng-Robinson EoS with the cubic mixing rule proposed by Pongsiri and Viswanath (1989) and later corrected by Caballero and Estévez (1992). This mixing rule it is given by:

$$a_{mix}^{\;1/3} = \frac{y_1 \left(a_{11}M_1\right)^{1/3} + y_2 \left(a_{22}M_2\right)^{1/3}}{y_1 M_1^{1/3} + y_2 M_2^{1/3}} + \left(\sqrt{a_{11}a_{22}}\right)^{1/3} y_1 y_2 \left(1 - k_{12}\right) \tag{3-5}$$

where M_i is the molar mass of component i. The term b_{mix} is calculated using the conventional van der Waals mixing rule, equation (2-15).

3.4 Patel-Teja Model with van der Waals Mixing Rules

The Cubic EoS Patel-Teja, is given by:

$$P = \frac{RT}{V-b} - \frac{a}{V\left(V+b\right) + c\left(V-b\right)} \tag{3-6}$$

where a is a function of temperature and b and c are constants:

$$a = \Omega_a \left(\frac{R^2 T_c^2}{P_c}\right)\left[1 + F\left(1 - \sqrt{T_r}\right)\right]^2 \tag{3-7}$$

$$b = \Omega_b \left(\frac{RT_c}{P_c}\right) \tag{3-8}$$

$$c = \Omega_c \left(\frac{RT_c}{P_c}\right) \tag{3-9}$$

where

$$\Omega_c = 1 - 3\xi_c \qquad \textbf{(3-10)}$$

$$\Omega_a = 3\xi_c^2 + 3(1 - 2\xi_c)\Omega_b + \Omega_b^2 + 1 - 3\xi_c \qquad \textbf{(3-11)}$$

and Ω_b is the smallest positive root of the cubic equation:

$$\Omega_b^3 + (2 - 3\xi_c)\Omega_b^2 + 3\xi_c^2\Omega_b - 3\xi_c^3 = 0 \qquad \textbf{(3-12)}$$

F and ξ_c are functions of the acentric factor given by the following correlations:

$$F = 0.452413 + 1.30982\omega - 0.295937\omega^2 \qquad \textbf{(3-13)}$$

$$\xi_c = 0.329032 - 0.076799\omega + 0.02119477\omega^2 \qquad \textbf{(3-14)}$$

Again, the van der Waals mixing rules have been described in Chapter 2, equations (2-11) until (2-15).

4. NEW COMBINATION RULE

4.1 Rationale

In general, mixing rules refer to the way the mixture parameters of any EoS are related to the pure-component parameters. This relationship is normally expressed by two equations: one relating the mixture parameter in terms of binary parameters (e.g., a_{mix} in terms of a_{ij} and mole fractions) and another relating the binary parameters to pure-component parameter. The second one is independent of composition and is normally refer to as combination rule. In this work, a new combination rule is proposed for parameter a of the EoS (any EoS) in binary systems. The approach is as follows. An "experimental" value of a_{12} is computed from the experimental solubility data. (One value of a_{12} is obtained for each data point in a given isotherm within the available database containing 126 isotherms.) To simplify this calculation, infinite dilution is assumed, i.e., $y_1 = 1$, $y_2 = 0$, and $Z = Z_{solvent}$. Then, for each isotherm, a correlation of a_{12} with reduced pressure is obtained. Finally, the parameters in that correlation are in turns correlated to reduced temperature and the a_2-to-a_1 ratio. This overall approach is better explained below.

For the development of this new combination rule, an existing database assembled by this research group over the years was used. The database contains 126 isotherms composed of five solvents (chlorotrifluoromethane, carbon dioxide, ethane, ethylene, and fluoroform) and twelve solutes (benzoic acid, fluorine, naphthalene, 2,3-dimethylnaph-thalene, 2,6-dimethylnaphthalene, 1,4-naphthoquinone, hexamethylbenzene, anthracene,

phenanthrene, acridine, hexachloroethane, and triphenylmethane). Half of the database (i.e., 63 isotherms) was used to develop the combination rule including the corresponding correlations. The other half was used to validate the correlations. A representative sample of the solute and solvent combinations were included in the 63 isotherms chosen to develop the combination rule. The values of a_{11} and a_{22} corresponding to the pure components in the mixture were calculated with equation (2-2) for each isotherm. The parameter a_{12} was obtained from the experimental data as described above, with a value of zero for the binary interaction parameters k_{ij}. These values were plotted with respect to the reduced pressure. For example, the system anthracene and carbon dioxide has been studied by different authors. The corresponding "experimental" values of a_{12} for the Peng-Robinson EoS are shown in Figures 4-1 and 4-2 at two temperatures. As observed, a_{12} varies (decreases for most systems) with pressure and approaches the van der Waals value ($\sqrt{a_1 a_2}$) at high pressures. These trends definitely indicate that the approach is promising. A detailed study was conducted both for the Peng-Robinson and for Patel-Teja EoS with van der Waals mixing rules, modified as proposed above.

The following dimensionless parameters were defined to normalize the values of a_{12}:

$$\xi = \frac{a_{12} - a_{11}}{a_{22} - a_{11}} \qquad (4\text{-}1)$$

$$\psi = \frac{a_{22}}{a_{11}} \qquad (4\text{-}2)$$

These definitions allowed representing all systems in one graph.
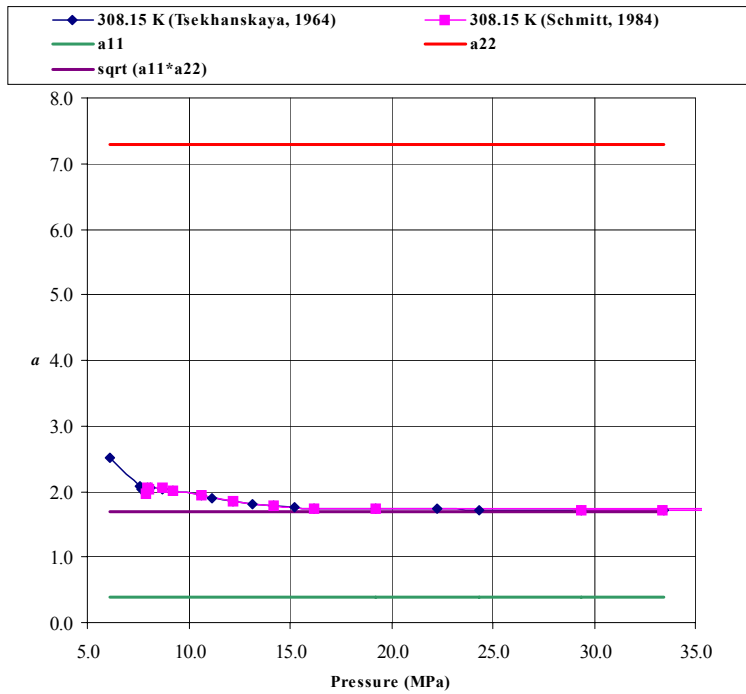
Figure 4-1. a_{12} **for Anthracene in Carbon Dioxide at 308.15 K**
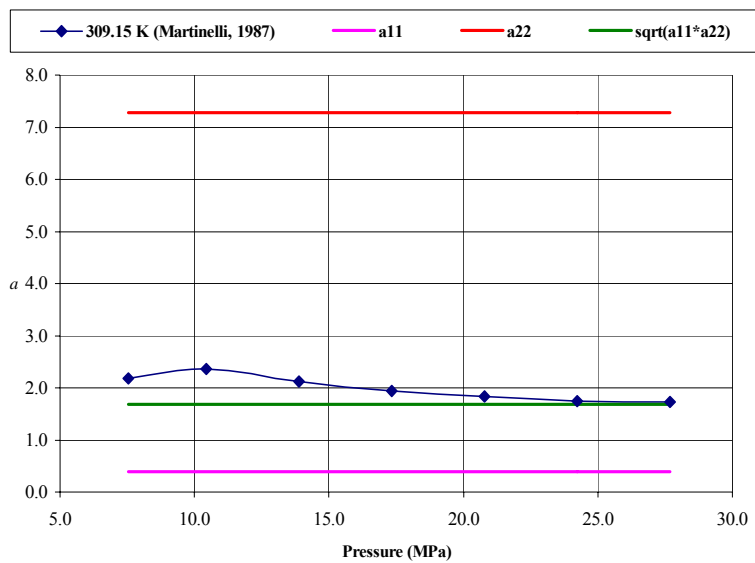
Figure 4-2. a_{12} **for Anthracene in Carbon Dioxide at 309.15 K**

4.2   Analysis for the Peng-Robinson EoS

Figure 4-3 shows a plot of ξ versus $1/P_r$ for the 63 isotherms selected to develop the correlation for the Peng-Robinson EoS. The $1/P_r$ dependency was used looking for a linear relationship. The temperatures ranged from 12 to 85 [°C].
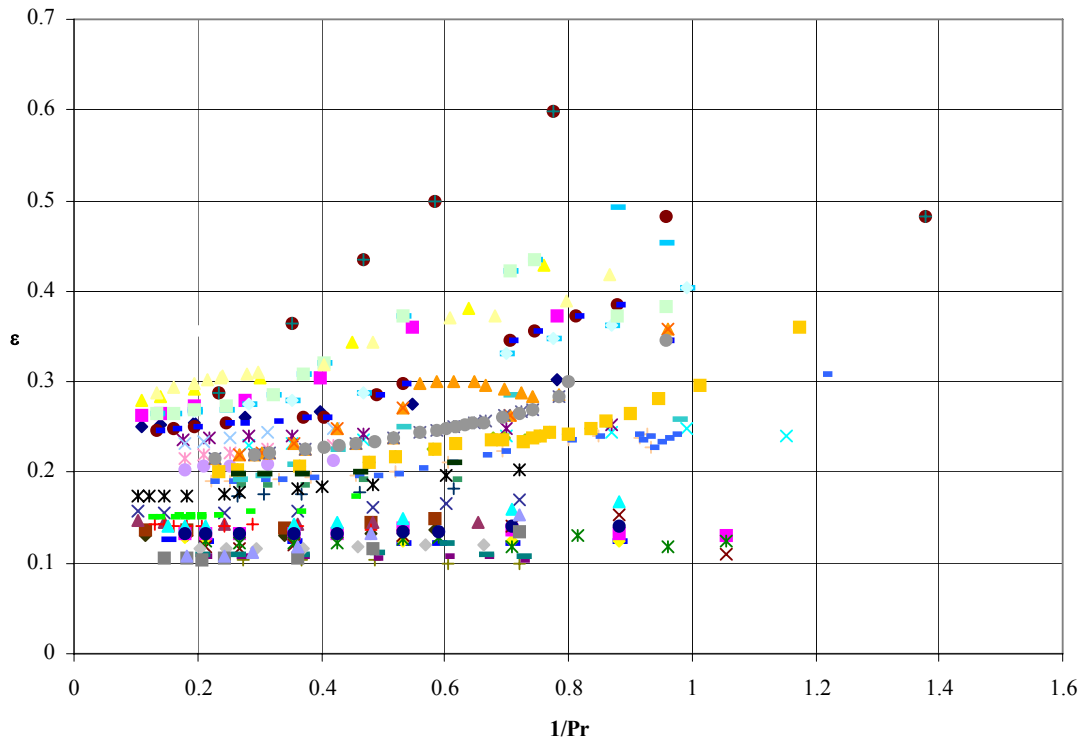
Figure 4-3. Values of ξ versus $1/P_r$, for 63 Systems Studied

For each system, a regression was sought between ξ and the reciprocal of the reduced pressure, as follows:

$$\xi = C_0 + C_1\left(\frac{1}{P_r}\right)$$ **(4-3)**

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Therefore, a group of 63 values of C_0 and C_1 were obtained. Relationships among these variables were sought using the program Minitab. These relationships were expressed in the following form:

$$C_0 = p_0 + p_1\psi + p_2 T_r \qquad\qquad (4\text{-}4)$$

$$C_1 = q_0 + q_1\psi + q_2 T_r \qquad\qquad (4\text{-}5)$$

For the Peng-Robinson EoS, the regression analysis for C_0 is presented in Table 4.1, which shows the parameters for the model:

Table 4-1. Regression Analysis: C_0 Versus ψ and T_r

Predictor	Coefficients	SE Coefficient	T	P-value
p_0	0.13448	0.09073	1.48	0.144
p_1	-0.00378	0.000503	-7.52	0
p_2	0.12	0.08649	1.39	0.17

In addition to the statistical analysis, the program Minitab display the quantity "R-squared" (R^2) defined as the proportion of the variability in the data explained by the model. A modification this value is the "adjusted R^2" ($R^2{}_{(adj)}$), that reflects an adjustment related to the number of the factors in the model. The values of these variables are in Table 4-2.

Table 4-2. Comparison of the R^2 Values for C_0 versus ψ and T_r

R^2	$R^2{}_{(adj)}$
48.6%	46.9%

Table 4-3 shows the analysis of variance for the variable C_0,

Table 4-3. Analysis of Variance for C_0 versus ψ and T_r

Source of Variation	Degrees of Freedom	Sum of Square	Mean Square	F_0	P-value
Regression	2	0.093654	0.046827	28.39	0
Residual Error	60	0.098952	0.001649		
Total	62	0.192605			

The value of R^2 is low and can be increased by making a transformation to the values of C_0, The tool Box-Cox plot, shown in the Figure 4-4, helped determine the most appropriate transformation.
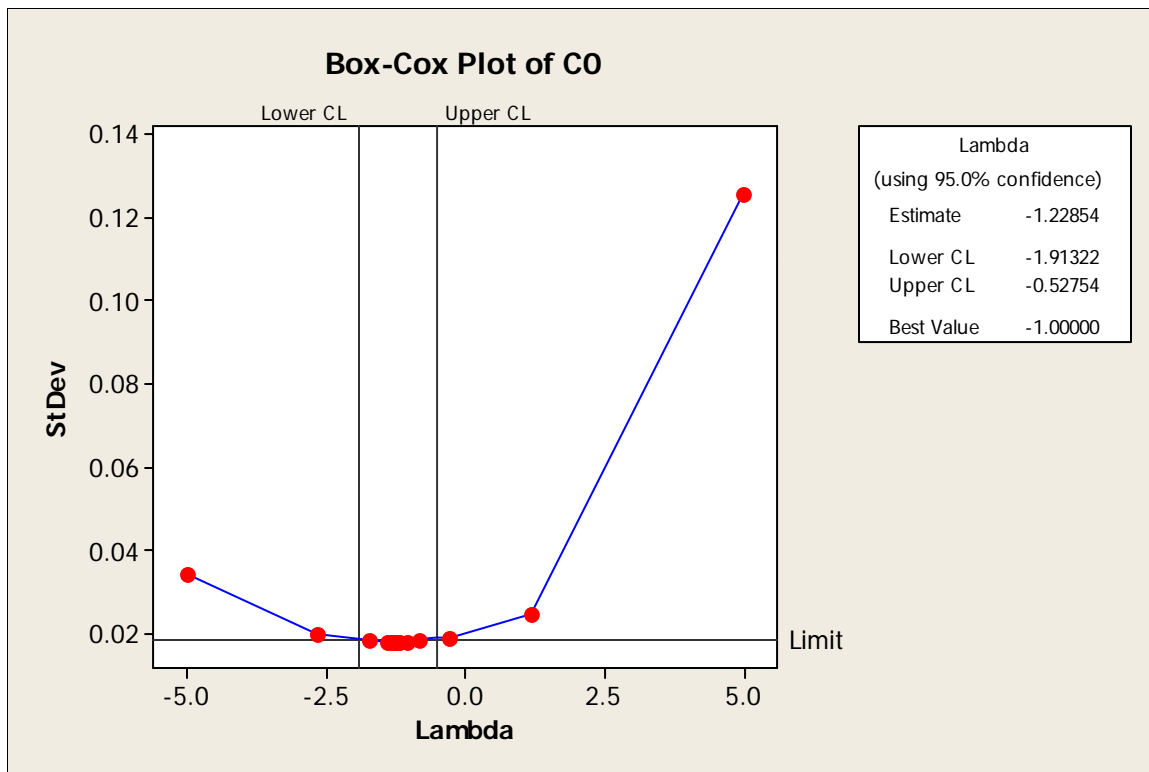
Figure 4-4. Box-Cox Plot for the Constant C_0

The suggested value is -1; this means that C_0 should be raised to this value (-1). Tables 4-4 and 4-6 present the results of the statistical analysis for the regression using this transformation. It can be seen that the value of R^2 improved from 48.6% to 76.1% and all parameters are statistically significant.

Table 4-4. Regression Analysis: Transformed C_0 versus ψ and T_r

Predictor	Coefficients	SE Coefficients	T	P-value
p_0	7.951	2.048	3.88	0
p_1	0.15648	0.01136	13.77	0
p_2	−5.013	1.952	−2.57	0.013

Table 4-5. Comparison of Values R^2 for Transformed C_0 versus ψ and T_r

R^2	$R^2_{\text{(adj)}}$
76.1%	75.3%

Table 4-6. Analysis of Variance for Transformed C_0 versus ψ and T_r

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F_0	P-value
Regression	2	160.136	80.068	95.31	0
Residual Error	60	50.403	0.84		
Total	62	210.539			

Therefore, the relationship among the variables ψ, T_r, y C_0, would be expressed as follows:

$$C_0^{-1} = \frac{1}{C_0} = p_0 + p_1\psi + p_2 T_r$$

$$C_0 = \frac{1}{p_0 + p_1\psi + p_2 T}$$

Replacing the values from Table 4-4, the equation for C_0 becomes:

$$C_0 = \frac{1}{7.951 + 0.15648\psi + -5.013T} \tag{4-6}$$

For C_1, the regression analysis is summarized in Tables 4-7 through 4-9

Table 4-7. Regression Analysis: C_1 versus ψ and T_r

Predictor	Coefficients	SE Coefficients	T	P-value
q_0	0.0727	0.1365	0.53	0.596
q_1	−0.00308	0.000757	−4.07	0
q_2	0.0548	0.1301	0.42	0.675

Table 4-8. Comparison of the R^2 Values for C_1 versus ψ and T_r

R^2	$R^2_{(adj)}$
22%	19.4%

Table 4-9. Analysis of Variance for C_1 versus ψ and T_r

Source of Variation	Degrees of Freedom	Sum of Square	Mean Square	F_0	P-value
Regression	2	0.063293	0.031647	8.48	0.001
Residual Error	60	0.223886	0.003731		
Total	62	0.287179			

Again, the value of R^2 is low, and the variable T_r is not significant for the model, therefore is eliminated of the model and a transformation to the other variable increasing the value of R^2. Tables 4-10 through 4-12 present the statistical analysis for the regression using with this transformation.

Table 4-10. Regression Analysis: (Transformed ψ) C_1 versus $1/\sqrt{\psi}$ and T_r

Predictor	Coefficients	SE Coefficients	T	P-value
q_0	−0.11144	0.03501	−3.18	0.002
q_1	0.7746	0.1583	4.89	0

Table 4-11. Comparison of the R^2 Values for Transformed C_1 versus ψ and T_r

R^2	$R^2_{(adj)}$
28.2%	27%

Table 4-12. Analysis of Variance for Transformed C_1 versus ψ and T_r

Source of Variation	Degrees of Freedom	Sum of Square	Mean Square	F_0	P-value
Regression	1	0.080924	0.080924	23.93	0
Residual Error	61	0.206255	0.003381		
Total	62	0.287179			

The relationship for C_1 in terms of ψ and T_r can be thus expressed as follows:

$$C_1 = q_0 + q_1 \frac{1}{\sqrt{\psi}}$$

Replacing the values from Table 4-10, C_1 becomes:

$$C_1 = q_0 + q_1 \frac{1}{\sqrt{\psi}} \qquad \textbf{(4-7)}$$

Therefore, the new combination rule for the Peng-Robinson EoS is given by the following equations:

$$a_{12} = \left[a_{11} + \xi \left(a_{22} - a_{11} \right) \right] \left(1 - k_{12} \right) \qquad \textbf{(4-8)}$$

$$\xi = C_0 + C_1 \left(\frac{1}{P_r} \right) \qquad \textbf{(4-9)}$$

$$C_0 = \left(56.4 + 2.41\psi - 66.5T_r\right)^{-0.5}$$

(4-10)

$$C_1 = \left(0.263 - 0.00534\psi + 0.097T_r\right)^2$$

(4-11)

$$\psi = \frac{a_{22}}{a_{11}}$$

(4-12)

4.3 Analysis for the Patel-Teja EoS

For Patel-Teja, the procedure is similar to the one described above. The regression analysis for C_0 is presented in Table 4.13.

Table 4-13. Regression Analysis: C_0 versus $1/\psi$ and T_r

Predictor	Coefficients	SE Coefficient	T	P-value
p_0	−0.12244	0.09057	−1.35	0.181
p_1	2.099	0.2346	8.95	0
p_2	0.17726	0.08024	2.21	0.031

The values of variables R^2 and $R^2_{(adj)}$ are shown in Table 4-14.

Table 4-14. Comparison of Values R^2 for C_0 versus ψ and T_r

R^2	$R^2_{(adj)}$
57.3%	55.8%

The analysis of variance for the variable C_0 is shown in Table 4-15.

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Table 4-15. Analysis of Variance for C_0 versus ψ and T_r

Source of Variation	Degrees of Freedom	Sum of Square	Mean Square	F_0	P-value
Regression	2	0.110289	0.055144	40.19	0
Residual Error	60	0.082316	0.001372		
Total	62	0.192605			

Therefore, the relationship among the variables $1/\psi$, T_r, and C_0, would be expressed as follows:

$$C_0 = p_0 + p_1 \frac{1}{\psi} + p_2 T_r$$

Replacing the values from Table 4-13, the equation for C_0 be comes:

$$C_0 = -0.12244 + 2.099 \frac{1}{\psi} + 0.17726 T_r \qquad \textbf{(4-13)}$$

For C_1, the regression analysis is summarized in Tables 4-10 through 4-21.

Table 4-16. Regression Analysis: C_1 Versus ψ and T_r

Predictor	Coefficients	SE Coefficients	T	P-value
q_0	0.0727	0.1365	0.53	0.596
q_1	-0.00308	0.000757	-4.07	0
q_2	0.0548	0.1301	0.42	0.675

Table 4-17. Comparison of Values R^2 for C_1 versus ψ and T_r

R^2	$R^2_{(adj)}$
22%	19.4%

Table 4-18. Analysis of Variance for C_1 versus ψ and T_r

Source of Variation	Degrees of Freedom	Sum of Square	Mean Square	F_0	P-value
Regression	2	0.063293	0.031647	8.48	0.001
Residual Error	60	0.223886	0.003731		
Total	62	0.287179			

The value of R^2 is low and can be increased by making a transformation to the values of C_1, before the transformation is added a constant from 0.2 to the values of C_1. The tool Box-Cox plot, shown in the Figure 4-5 helped determine the most appropriate transformation:
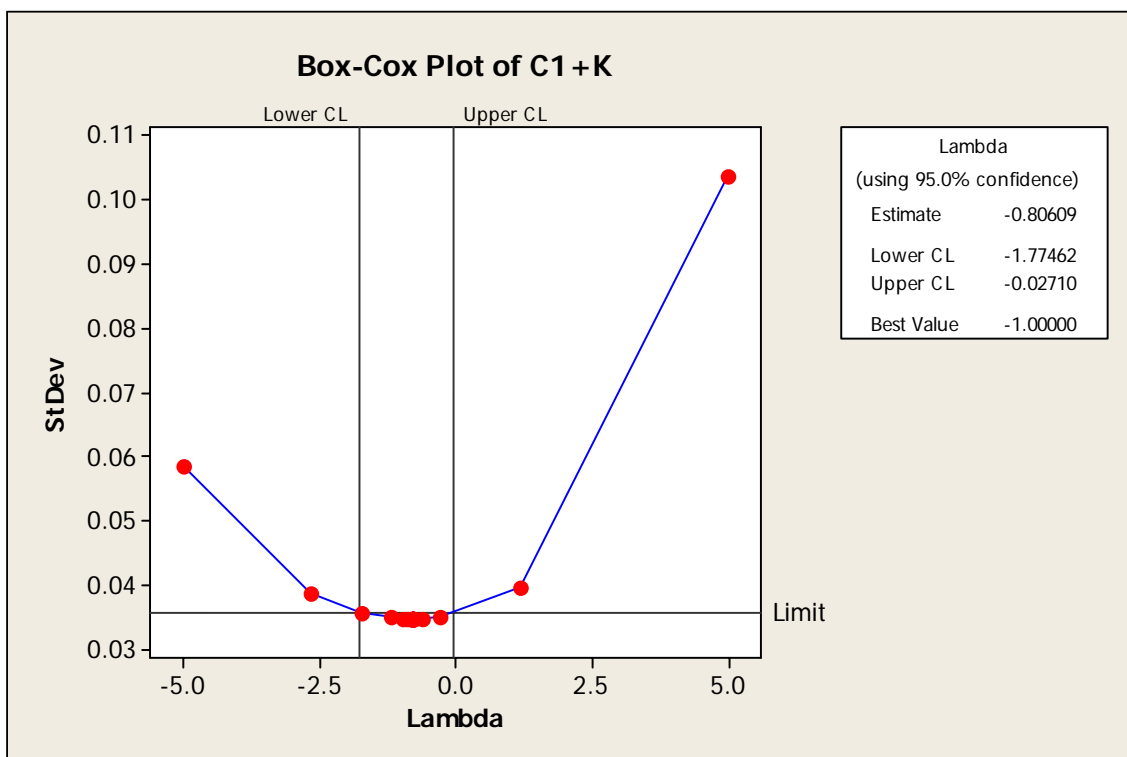
Figure 4-5. Box-Cox Plot for the Constant C_1

The relationship for C_1 in terms of ψ and T_r can be thus expressed as follows:

$$\left(C_1 + 0.2\right)^{-1} = q_0 + q_1 \frac{1}{\psi} + q_2 \frac{1}{T_r}$$

$$C_1 = \left(\frac{1}{q_0 + q_1 \dfrac{1}{\psi} + q_2 \dfrac{1}{T_r}}\right) - 0.2$$

Replacing the values from Minitab, C_1 becomes:

$$C_1 = \left(\frac{1}{1.703 - 32.258 \dfrac{1}{\psi} + 4.194 \dfrac{1}{T_r}}\right) - 0.2 \qquad \textbf{(4-14)}$$

Therefore, the new combination rule for the Patel-Teja EoS is given by the following equations:

$$a_{12} = \left[a_{11} + \xi\left(a_{22} - a_{11}\right)\right]\left(1 - k_{12}\right) \qquad \textbf{(4-15)}$$

$$\xi = C_0 + C_1\left(\frac{1}{P_r}\right) \qquad \textbf{(4-16)}$$

$$C_0 = -0.12244 + 2.099\frac{1}{\psi} + 0.17726 T_r \qquad \textbf{(4-17)}$$

$$C_1 = \left(\frac{1}{1.703 - 32.258 \dfrac{1}{\psi} + 4.194 \dfrac{1}{T_r}}\right) - 0.2 \qquad \textbf{(4-18)}$$

$$\psi = \frac{a_{22}}{a_{11}} \qquad \textbf{(4-19)}$$

5. RESULTS

5.1   Overview

This Chapter presents the results obtained in this work. The results are mainly based on error (AVERR) calculated according to equation (2-29) but also contains predictive capacity results.   Different thermodynamics models described in Chapter 4 were analyzed. For each model, AVERR was computed for every isotherm. Isotherms were separated in two groups.   Group 1 contains the 63 isotherms used to obtain the correlations presented in Chapter 4 while Group 2 contains the rest of the isotherms. Then, the values of AVERR were averaged within each of these groups or the two groups in some cases were lumped together.

5.2   Errors for Various Models

To have an overall view of the results, Figure 5-1 was prepared. It shows the averaged AVERR for all 126 isotherms (i.e., the two groups described above lumped together) for various models. It is observed there that Patel-Teja with the new mixing rule (NMR) gives the best results. Moreover, a comparison of the average errors for the Peng-Robinson EoS with different mixing rules gives values between a 20.2 and 28.6%. The largest error corresponded to the Rao mixing rule (28.6%) followed by the cubic mixing rule (26.0%) and van der Waals mixing rule (20.2%). Figure 5-1 also shows, for the van der Waals mixing rule, a comparison of the Peng-Robinson and Patel-Teja EoS.

As seen, the Patel-Teja EoS was better (16.4%) than the Peng-Robinson EoS (20.2% error).
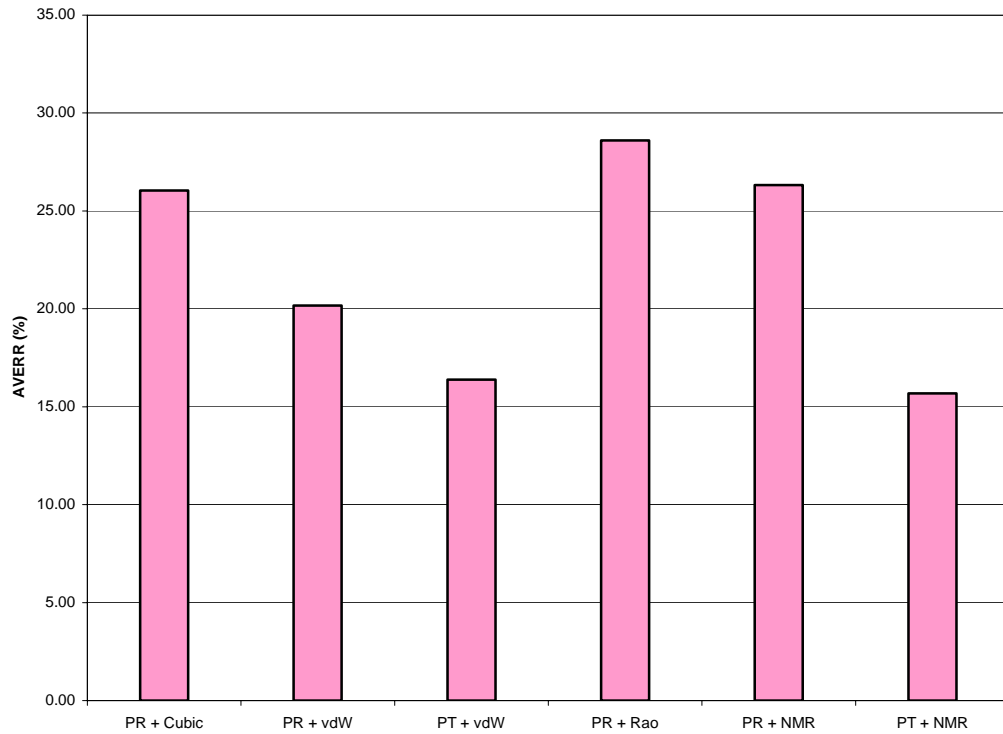
Figure 5-1. Comparison of the Different Thermodynamic Models

In Figure 5-2, the errors for four of the models are compared by groups. It is interesting to note that in all cases the error for Group 2 are smaller than those of Group 1 when one would expect the opposite to occur. When all the isotherms are taken into account, the model Patel-Teja + new mixing rule results in the smallest error.
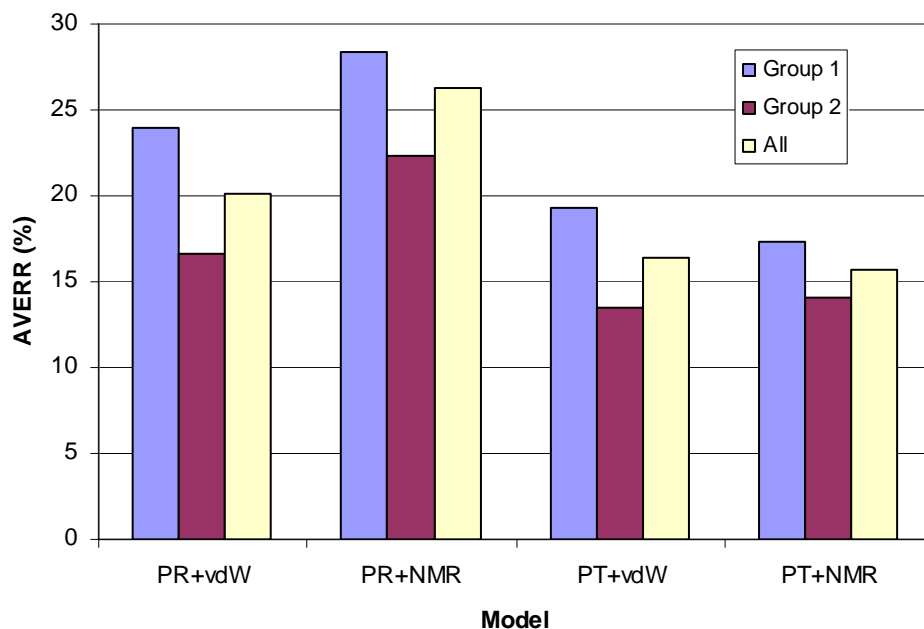
Figure 5-2. Summary of Errors by Model and by Data Group.

A detail tabulation of the errors is given in Appendix B. A sample code of the various Matlab programs written to carry out the calculations in this thesis is presented in Appendix C.

5.3   Predictive Capacity

It is interesting to compare the predictive capacity of the various models. To this end, Figure 5-3 has been prepared. It shows the experimental solubility of acridine in carbon dioxide at 318.15 [K] and the predictions using various models. The Patel-Teja

EoS with the new mixing rule works best in this task. Interestingly, all models in that Figure have a similar capacity at high pressures. However, at low pressures, the Patel-Teja + NMR model is able to fit better the experimental data, although it underestimates them. The rest of the models overestimate the solubility at low pressures.
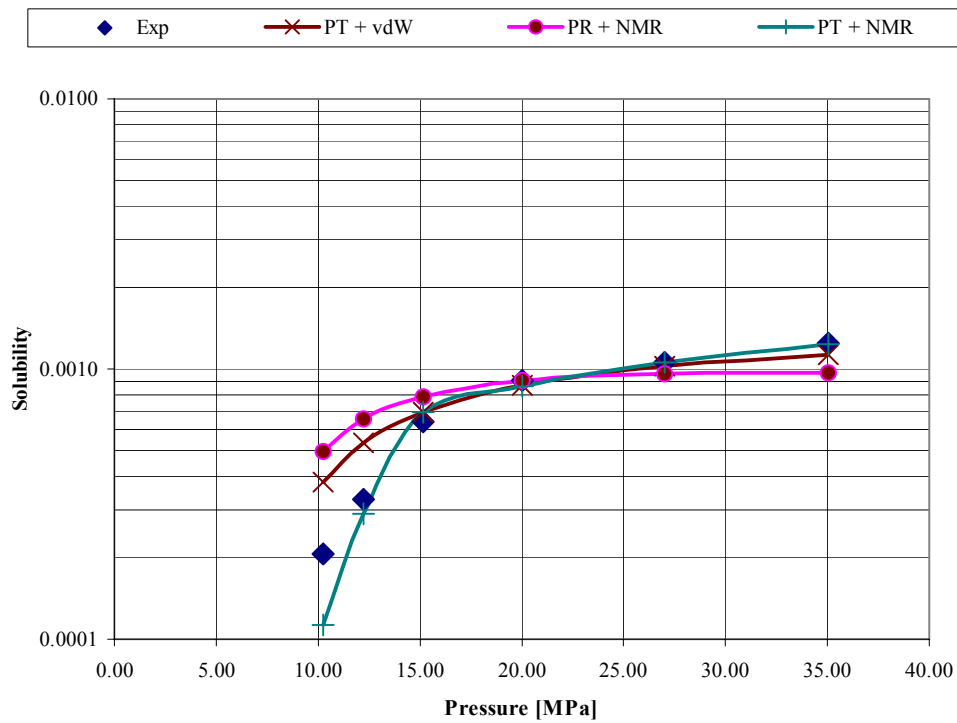
Figure 5-3. Solubility of Acridine in Carbon Dioxide using the van der Waals Mixing Rule

6. CONCLUSIONS

A new combination rule has been proposed to be used in the modeling and estimation of solubility of solids in supercritical fluids. The proposed rule is a modification of the classical van der Waals mixing rules where the binary cohesive parameter of the EoS (any EoS) is allow to vary with pressure. Correlations for the proposed mixing rule were developed for the Peng-Robinson and Patel-Teja EoS based on the experimental data of sixty-three isotherms. The correlations were then applied to the rest of the isotherms with very good results.

Different thermodynamic models were compared, using different cubic equations of state, such as Peng-Robinson and Patel-Teja, and different mixing rules such as van der Waals, Rao, and cubic. These models are the most widely used in the calculation of the solubility of solids in supercritical fluids. The model that best fits the experimental values is the composed of the Patel-Teja equation and the van der Waals mixing rule.

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APPENDIX A. ANALYTICAL SOLUTION OF CUBIC EQUATIONS

This Appendix presents the analytical solution of cubic polynomial equations written in the following form:

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

First, let:

$$Q \equiv \frac{3p_2 - p_1}{9}; \quad R \equiv \frac{9p_1 p_2 - 27 p_3 - 2p_1^3}{54} \quad \text{and} \quad D^* \equiv Q^3 + R^2 \tag{A-2}$$

D^* is called the discriminant and its value determines the domain of the roots to Equation (A-2): (1) if $D^* < 0$, all roots are real and different; (2) if $D^* = 0$, all roots are real and at least two are equal; and (3) if $D^* > 0$, only one root is real and two are conjugate complex.

For $D^* > 0$, the real root is given by:

$$X_1 = S + T - \frac{1}{3} p_1 \tag{A-3}$$

and the two complex roots $\left(i \equiv \sqrt{-1} \right)$ are:

$$X_{2,3} = -\frac{1}{2}(S+T) - \frac{1}{3} p_1 \pm \frac{1}{2} i\sqrt{3}(S-T) \tag{A-4}$$

where

$$S = \left(R + \sqrt{D^*} \right)^{1/3} \quad \text{and} \quad T = \left(R - \sqrt{D^*} \right)^{1/3} \tag{A-5}$$

If $D^* = 0$, then $S = T$ and the imaginary components vanish so 3 real roots result.
For $D^* < 0$, the roots are given by:

$$X_1 = 2\sqrt{-Q}\cos\left(\frac{\Theta}{3}\right) - \frac{1}{3}p_1 \qquad\qquad \text{(A-6)}$$

$$X_2 = 2\sqrt{-Q}\cos\left(\frac{\Theta}{3} + 120^o\right) - \frac{1}{3}p_1 \qquad\qquad \text{(A-7)}$$

$$X_3 = 2\sqrt{-Q}\cos\left(\frac{\Theta}{3} + 240^o\right) - \frac{1}{3}p_1 \qquad\qquad \text{(A-8)}$$

where

$$\cos\Theta = \frac{R}{\sqrt{-Q^3}} \qquad\qquad \text{(A-9)}$$

APPENDIX B. DETAILED ERROR TABULATION

Table B-1. Calculated Error with of Peng-Robinson EOS with Different Mixing Rule

No.	Solute	Solvent	Temp.(°C)	AVERR			
				PR + Cubic	PR + vdW	PR + Rao	PR + NMR
1	Acridine	Carbon Dioxide	35	22.97	25.00	59.07	8.69
2	Acridine	Carbon Dioxide	45	7.26	10.05	20.30	9.97
3	Acridine	Carbon Dioxide	55	28.97	29.96	30.35	27.49
4	Acridine	Carbon Dioxide	70	31.41	14.37	24.05	18.58
5	Acridine	Chlorotrifluoromethane	45	9.68	6.05	57.56	17.36
6	Acridine	Chlorotrifluoromethane	55	13.21	6.06	25.57	20.37
7	Acridine	Ethane	35	13.90	12.61	48.13	14.44
8	Acridine	Ethane	55	22.45	13.35	39.18	29.00
9	Acridine	Ethane	70	14.77	5.27	30.39	18.41
10	Acridine	Fluoroform	45	11.00	9.24	28.92	18.93
11	Acridine	Fluoroform	55	16.49	11.32	33.96	25.97
12	Anthracene	Carbon Dioxide	30	48.16	48.65	58.69	13.61
13	Anthracene	Carbon Dioxide	35	38.26	38.68	56.62	5.79
14	Anthracene	Carbon Dioxide	45	19.04	19.14	59.60	7.44
15	Anthracene	Carbon Dioxide	50	21.08	22.14	28.87	24.42
16	Anthracene	Carbon Dioxide	70	31.18	25.48	35.60	27.15
17	Anthracene	Ethane	30	28.68	29.40	48.48	34.28
18	Anthracene	Ethane	35	32.52	32.79	61.40	44.38
19	Anthracene	Ethane	50	20.69	21.18	56.70	45.03
20	Anthracene	Ethane	70	11.37	11.37	45.51	30.61
21	Anthracene	Ethylene	50	20.11	20.49	40.92	32.45
22	Anthracene	Ethylene	70	29.38	26.78	35.53	33.49

No.	Solute	Solvent	Temp.(°C)	AVERR			
				PR + Cubic	PR + vdW	PR + Rao	PR + NMR
23	Anthracene	Ethylene	85	28.58	20.72	9.94	27.68
24	Benzoic Acid	Carbon Dioxide	45	11.82	5.45	28.92	24.02
25	Benzoic Acid	Carbon Dioxide	55	10.21	5.45	5.38	19.99
26	Benzoic Acid	Carbon Dioxide	65	9.08	5.46	3.47	17.30
27	Benzoic Acid	Ethylene	45	12.12	9.60	9.72	12.31
28	Benzoic Acid	Ethylene	55	17.36	4.77	4.61	8.72
29	Benzoic Acid	Ethylene	65	17.10	3.25	5.60	11.03
30	Fluorene	Carbon Dioxide	30	25.08	25.08	54.80	35.10
31	Fluorene	Carbon Dioxide	35	17.35	17.35	69.44	34.64
32	Fluorene	Carbon Dioxide	50	14.97	10.58	29.97	27.18
33	Fluorene	Carbon Dioxide	70	19.68	8.97	12.11	27.55
34	Fluorene	Ethylene	25	18.43	18.43	84.59	62.11
35	Fluorene	Ethylene	45	16.38	16.38	24.71	41.28
36	Fluorene	Ethylene	70	25.61	22.03	16.59	32.45
37	Hexamethylbenzene	Carbon Dioxide	30	59.07	57.85	43.23	37.69
38	Hexamethylbenzene	Carbon Dioxide	50	24.37	24.40	34.85	32.89
39	Hexamethylbenzene	Carbon Dioxide	70	29.13	20.14	28.90	34.82
40	Hexamethylbenzene	Ethylene	25	37.10	37.10	56.43	67.24
41	Hexamethylbenzene	Ethylene	45	24.99	24.99	55.88	54.88
42	Hexamethylbenzene	Ethylene	70	33.03	30.37	27.97	37.27
43	Hexachloroethane	Carbon Dioxide	35	4.72	5.18	5.52	45.68
44	Hexachloroethane	Carbon Dioxide	45	32.20	13.95	3.85	12.48
45	Hexachloroethane	Carbon Dioxide	55	67.77	43.14	45.01	38.86
46	2,3 - Dimethynaphthalene	Carbon Dioxide	45	7.01	4.22	32.85	28.57
47	2,3 - Dimethynaphthalene	Carbon Dioxide	55	19.24	10.33	15.38	16.16
48	2,3 - Dimethynaphthalene	Ethylene	35	4.37	4.41	16.29	23.10
49	2,3 - Dimethynaphthalene	Ethylene	45	10.77	9.35	6.04	16.64
50	2,3 - Dimethynaphthalene	Ethylene	55	21.33	7.62	10.41	21.31

No.	Solute	Solvent	Temp.(°C)	AVERR			
				PR + Cubic	PR + vdW	PR + Rao	PR + NMR
51	2,6 - Dimethynaphthalene	Carbon Dioxide	35	5.86	5.86	35.30	36.35
52	2,6 - Dimethynaphthalene	Carbon Dioxide	45	24.17	5.96	8.99	9.99
53	2,6 - Dimethynaphthalene	Carbon Dioxide	55	48.54	17.01	13.13	10.34
54	2,6 - Dimethynaphthalene	Ethylene	35	4.32	4.34	2.72	21.87
55	2,6 - Dimethynaphthalene	Ethylene	45	7.23	7.24	3.31	17.98
56	2,6 - Dimethynaphthalene	Ethylene	55	20.22	19.63	19.20	30.10
57	Naphthalene	Carbon Dioxide	35	242.44	241.57	241.76	34.93
58	Naphthalene	Carbon Dioxide	35	50.04	50.06	45.49	37.56
59	Naphthalene	Carbon Dioxide	36	64.14	43.76	21.78	27.99
60	Naphthalene	Carbon Dioxide	45	48.36	30.81	25.40	23.89
61	Naphthalene	Carbon Dioxide	45	59.27	47.63	29.79	28.38
62	Naphthalene	Carbon Dioxide	55	48.87	21.54	8.00	16.64
63	Naphthalene	Carbon Dioxide	55	42.02	22.26	8.43	13.05
64	Naphthalene	Carbon Dioxide	55	53.07	25.05	18.13	16.54
65	Naphthalene	Chlorotrifluoromethane	35	5.76	6.68	5.82	18.51
66	Naphthalene	Chlorotrifluoromethane	45	36.41	18.83	17.78	44.45
67	Naphthalene	Chlorotrifluoromethane	55	20.44	18.05	8.78	18.19
68	Naphthalene	Ethane	20	12.28	14.42	12.31	11.55
69	Naphthalene	Ethane	25	3.88	5.88	3.64	81.57
70	Naphthalene	Ethane	35	85.93	66.12	53.15	81.47
71	Naphthalene	Ethane	35	45.48	39.98	30.16	61.98
72	Naphthalene	Ethane	45	38.96	44.34	17.13	79.07
73	Naphthalene	Ethane	45	54.65	40.57	13.77	40.94
74	Naphthalene	Ethane	55	23.58	15.48	52.41	31.31
75	Naphthalene	Ethylene	12	4.50	1.69	1.53	20.70
76	Naphthalene	Ethylene	12	47.99	44.32	34.95	29.71
77	Naphthalene	Ethylene	25	2.65	4.36	2.85	10.19
78	Naphthalene	Ethylene	25	78.77	25.04	11.55	25.11

No.	Solute	Solvent	Temp.(°C)	AVERR			
				PR + Cubic	PR + vdW	PR + Rao	PR + NMR
79	Naphthalene	Ethylene	25	31.53	27.04	15.76	45.01
80	Naphthalene	Ethylene	35	2.58	5.89	2.35	29.26
81	Naphthalene	Ethylene	35	24.21	10.78	5.17	22.81
82	Naphthalene	Ethylene	45	30.40	31.98	15.72	25.58
83	Naphthalene	Ethylene	45	15.62	11.24	5.83	25.26
84	Naphthalene	Ethylene	45	11.37	12.00	10.32	11.42
85	Naphthalene	Ethylene	50	34.28	17.33	75.41	19.77
86	Naphthalene	Ethylene	50	14.35	10.38	23.91	8.28
87	Naphthalene	Ethylene	60	0.01	0.04	88.17	75.31
88	Naphthalene	Fluoroform	35	37.60	28.54	34.19	6.48
89	Naphthalene	Fluoroform	45	35.64	20.63	19.72	12.51
90	Naphthalene	Fluoroform	55	28.40	23.97	9.42	17.29
91	1,4 - Naphthoquinone	Carbon Dioxide	45	19.85	18.74	29.57	44.41
92	1,4 - Naphthoquinone	Carbon Dioxide	55	19.85	9.39	18.39	5.11
93	1,4 - Naphthoquinone	Carbon Dioxide	70	5.69	10.83	4.16	0.13
94	1,4 - Naphthoquinone	Chlorotrifluoromethane	45	22.39	19.57	33.27	28.37
95	1,4 - Naphthoquinone	Chlorotrifluoromethane	55	16.25	7.23	26.42	18.82
96	1,4 - Naphthoquinone	Ethane	35	12.09	14.10	52.88	11.10
97	1,4 - Naphthoquinone	Ethane	45	16.46	13.67	25.86	25.04
98	1,4 - Naphthoquinone	Ethane	55	25.60	16.20	30.88	17.25
99	1,4 - Naphthoquinone	Ethane	70	16.67	10.50	16.24	13.64
100	1,4 - Naphthoquinone	Fluoroform	45	18.63	12.38	18.78	25.68
101	1,4 - Naphthoquinone	Fluoroform	55	18.05	16.24	12.70	16.67
102	Phenanthrene	Carbon Dioxide	30	11.42	16.22	53.50	69.64
103	Phenanthrene	Carbon Dioxide	45	11.09	10.43	0.00	33.29
104	Phenanthrene	Carbon Dioxide	45	6.49	8.80	38.21	21.18
105	Phenanthrene	Carbon Dioxide	50	14.72	11.86	18.78	18.98
106	Phenanthrene	Carbon Dioxide	55	28.76	33.65	25.45	17.98

No.	Solute	Solvent	Temp.(°C)	AVERR			
				PR + Cubic	PR + vdW	PR + Rao	PR + NMR
107	Phenanthrene	Carbon Dioxide	55	13.31	11.63	19.63	28.03
108	Phenanthrene	Carbon Dioxide	65	18.03	8.84	15.11	59.23
109	Phenanthrene	Carbon Dioxide	70	18.32	15.42	16.53	14.52
110	Phenanthrene	Ethane	30	8.61	9.17	46.85	15.30
111	Phenanthrene	Ethane	40	3.52	7.90	29.87	11.46
112	Phenanthrene	Ethane	60	22.41	9.13	28.94	31.22
113	Phenanthrene	Ethylene	25	4.93	4.93	6.04	10.17
114	Phenanthrene	Ethylene	45	11.66	11.18	24.03	6.66
115	Phenanthrene	Ethylene	45	1.19	1.32	2.74	14.14
116	Phenanthrene	Ethylene	45	6.61	6.62	30.14	69.20
117	Phenanthrene	Ethylene	55	22.44	16.86	25.74	30.60
118	Phenanthrene	Ethylene	65	108.41	63.84	60.18	17.36
119	Phenanthrene	Ethylene	70	23.72	27.96	14.56	85.42
120	Phenanthrene	Ethylene	70	0.01	0.82	0.01	6.73
121	Triphenylmethane	Carbon Dioxide	30	38.06	28.35	30.88	61.83
122	Triphenylmethane	Carbon Dioxide	40	30.30	25.10	26.15	16.64
123	Triphenylmethane	Carbon Dioxide	50	8.49	11.67	10.07	2.22
124	Triphenylmethane	Ethylene	30	19.35	21.02	34.89	24.92
125	Triphenylmethane	Ethylene	40	35.96	20.34	33.54	26.27
126	Triphenylmethane	Ethylene	50	64.10	14.12	21.97	69.70

Table B-2. Comparison of the van der Waals Mixing Rule with Different Equation of State

No.	Solute	Solvent	Temp.(°C)	k_{12}		AVERR	
				PT + vdW	PR + vdW	PT + vdW	PR + vdW
1	Acridine	Carbon Dioxide	35	0.218	0.200	16.96	25.00
2	Acridine	Carbon Dioxide	45	0.200	0.174	5.86	10.05
3	Acridine	Carbon Dioxide	55	0.210	0.152	20.54	29.96
4	Acridine	Carbon Dioxide	70	0.160	0.140	9.23	14.37
5	Acridine	Chlorotrifluoromethane	45	0.260	0.220	4.33	6.05
6	Acridine	Chlorotrifluoromethane	55	0.250	0.200	7.06	6.06
7	Acridine	Ethane	35	0.240	0.210	14.80	12.61
8	Acridine	Ethane	55	0.150	0.140	11.14	13.35
9	Acridine	Ethane	70	0.110	0.100	5.43	5.27
10	Acridine	Fluoroform	45	0.260	0.210	7.33	9.24
11	Acridine	Fluoroform	55	0.220	0.170	10.34	11.32
12	Anthracene	Carbon Dioxide	30	0.230	0.220	45.69	48.65
13	Anthracene	Carbon Dioxide	35	0.220	0.210	36.80	38.68
14	Anthracene	Carbon Dioxide	45	0.200	0.190	17.82	19.14
15	Anthracene	Carbon Dioxide	50	0.180	0.170	20.67	22.14
16	Anthracene	Carbon Dioxide	70	0.130	0.130	24.08	25.48
17	Anthracene	Ethane	30	0.180	0.180	26.31	29.40
18	Anthracene	Ethane	35	0.170	0.170	29.53	32.79
19	Anthracene	Ethane	50	0.130	0.130	19.69	21.18
20	Anthracene	Ethane	70	0.060	0.070	10.94	11.37
21	Anthracene	Ethylene	50	0.110	0.110	18.17	20.49
22	Anthracene	Ethylene	70	0.100	0.090	24.65	26.78
23	Anthracene	Ethylene	85	0.070	0.080	20.23	20.72
24	Benzoic Acid	Carbon Dioxide	45	0.070	0.035	6.36	5.45
25	Benzoic Acid	Carbon Dioxide	55	0.000	-0.025	4.87	5.45
26	Benzoic Acid	Carbon Dioxide	65	-0.050	-0.073	4.24	5.46

No.	Solute	Solvent	Temp.(°C)	k_{12}		AVERR	
				PT + vdW	PR + vdW	PT + vdW	PR + vdW
27	Benzoic Acid	Ethylene	45	-0.010	-0.016	10.19	9.60
28	Benzoic Acid	Ethylene	55	-0.050	-0.051	5.52	4.77
29	Benzoic Acid	Ethylene	65	-0.110	-0.109	3.59	3.25
30	Fluorene	Carbon Dioxide	30	0.140	0.126	20.05	25.08
31	Fluorene	Carbon Dioxide	35	0.130	0.113	13.67	17.35
32	Fluorene	Carbon Dioxide	50	0.100	0.082	8.62	10.58
33	Fluorene	Carbon Dioxide	70	0.040	0.023	8.59	8.97
34	Fluorene	Ethylene	25	0.070	0.070	13.90	18.43
35	Fluorene	Ethylene	45	0.010	0.010	14.72	16.38
36	Fluorene	Ethylene	70	-0.080	-0.069	17.36	22.03
37	Hexamethylbenzene	Carbon Dioxide	30	0.930	0.183	23.43	57.85
38	Hexamethylbenzene	Carbon Dioxide	50	0.150	0.106	17.27	24.40
39	Hexamethylbenzene	Carbon Dioxide	70	0.090	0.057	14.88	20.14
40	Hexamethylbenzene	Ethylene	25	0.120	0.101	28.46	37.10
41	Hexamethylbenzene	Ethylene	45	0.050	0.039	20.12	24.99
42	Hexamethylbenzene	Ethylene	70	-0.010	-0.029	25.17	30.37
43	Hexachloroethane	Carbon Dioxide	35	-0.090	-0.065	4.46	5.18
44	Hexachloroethane	Carbon Dioxide	45	-0.280	-0.213	14.23	13.95
45	Hexachloroethane	Carbon Dioxide	55	-0.340	-0.382	43.00	43.14
46	2,3 - Dimethynaphthalene	Carbon Dioxide	45	0.130	0.116	3.06	4.22
47	2,3 - Dimethynaphthalene	Carbon Dioxide	55	0.160	0.199	6.38	10.33
48	2,3 - Dimethynaphthalene	Ethylene	35	0.010	0.015	3.88	4.41
49	2,3 - Dimethynaphthalene	Ethylene	45	-0.030	-0.016	6.72	9.35
50	2,3 - Dimethynaphthalene	Ethylene	55	-0.080	-0.069	7.82	7.62
51	2,6 - Dimethynaphthalene	Carbon Dioxide	35	0.100	0.076	4.72	5.86
52	2,6 - Dimethynaphthalene	Carbon Dioxide	45	0.190	0.186	4.85	5.96
53	2,6 - Dimethynaphthalene	Carbon Dioxide	55	0.100	0.155	3.75	17.01
54	2,6 - Dimethynaphthalene	Ethylene	35	-0.020	-0.012	3.57	4.34
55	2,6 - Dimethynaphthalene	Ethylene	45	-0.070	-0.060	5.49	7.24

No.	Solute	Solvent	Temp.(°C)	k_{12}		AVERR	
				PT + vdW	PR + vdW	PT + vdW	PR + vdW
56	2,6 - Dimethynaphthalene	Ethylene	55	-0.140	-0.115	16.75	19.63
57	Naphthalene	Carbon Dioxide	35	0.090	0.095	241.61	241.57
58	Naphthalene	Carbon Dioxide	35	0.100	-0.021	50.49	50.06
59	Naphthalene	Carbon Dioxide	36	0.050	0.080	21.92	43.76
60	Naphthalene	Carbon Dioxide	45	0.000	0.000	27.92	30.81
61	Naphthalene	Carbon Dioxide	45	-0.070	-0.060	43.09	47.63
62	Naphthalene	Carbon Dioxide	55	-0.120	-0.140	7.74	21.54
63	Naphthalene	Carbon Dioxide	55	-0.130	-0.120	20.45	22.26
64	Naphthalene	Carbon Dioxide	55	-0.120	-0.090	7.00	25.05
65	Naphthalene	Chlorotrifluoromethane	35	-0.020	-0.010	5.94	6.68
66	Naphthalene	Chlorotrifluoromethane	45	-0.030	0.020	18.33	18.83
67	Naphthalene	Chlorotrifluoromethane	55	-0.120	-0.100	14.23	18.05
68	Naphthalene	Ethane	20	-0.020	0.000	12.38	14.42
69	Naphthalene	Ethane	25	-0.050	-0.030	3.97	5.88
70	Naphthalene	Ethane	35	-0.050	-0.060	61.09	66.12
71	Naphthalene	Ethane	35	-0.040	-0.020	33.03	39.98
72	Naphthalene	Ethane	45	-0.130	-0.160	27.87	44.34
73	Naphthalene	Ethane	45	-0.150	-0.140	22.00	40.57
74	Naphthalene	Ethane	55	-0.270	-0.300	11.90	15.48
75	Naphthalene	Ethylene	12	-0.040	-0.020	1.79	1.69
76	Naphthalene	Ethylene	12	0.030	0.160	39.82	44.32
77	Naphthalene	Ethylene	25	-0.090	-0.060	3.64	4.36
78	Naphthalene	Ethylene	25	-0.100	0.104	20.68	25.04
79	Naphthalene	Ethylene	25	-0.100	-0.030	20.50	27.04
80	Naphthalene	Ethylene	35	-0.150	-0.120	3.16	5.89
81	Naphthalene	Ethylene	35	-0.160	-0.130	6.33	10.78
82	Naphthalene	Ethylene	45	-0.210	-0.220	27.93	31.98
83	Naphthalene	Ethylene	45	-0.260	-0.230	3.54	11.24
84	Naphthalene	Ethylene	45	-0.240	-0.200	9.03	12.00

No.	Solute	Solvent	Temp.(°C)	k_{12}		AVERR	
				PT + vdW	PR + vdW	PT + vdW	PR + vdW
85	Naphthalene	Ethylene	50	-0.320	-0.350	17.39	17.33
86	Naphthalene	Ethylene	50	-0.310	-0.180	4.40	10.38
87	Naphthalene	Ethylene	60	-0.570	-0.495	0.01	0.04
88	Naphthalene	Fluoroform	35	0.130	0.140	28.60	28.54
89	Naphthalene	Fluoroform	45	0.050	0.050	20.63	20.63
90	Naphthalene	Fluoroform	55	-0.090	-0.090	11.57	23.97
91	1,4 - Naphthoquinone	Carbon Dioxide	45	0.120	0.070	19.21	18.74
92	1,4 - Naphthoquinone	Carbon Dioxide	55	0.090	0.040	2.76	9.39
93	1,4 - Naphthoquinone	Carbon Dioxide	70	0.030	0.000	5.92	10.83
94	1,4 - Naphthoquinone	Chlorotrifluoromethane	45	0.200	0.440	22.94	19.57
95	1,4 - Naphthoquinone	Chlorotrifluoromethane	55	0.220	0.190	3.12	7.23
96	1,4 - Naphthoquinone	Ethane	35	0.200	0.160	12.87	14.10
97	1,4 - Naphthoquinone	Ethane	45	0.220	0.170	14.00	13.67
98	1,4 - Naphthoquinone	Ethane	55	0.160	0.220	10.21	16.20
99	1,4 - Naphthoquinone	Ethane	70	0.090	0.070	6.01	10.50
100	1,4 - Naphthoquinone	Fluoroform	45	0.140	0.070	11.27	12.38
101	1,4 - Naphthoquinone	Fluoroform	55	0.040	0.000	15.68	16.24
102	Phenanthrene	Carbon Dioxide	30	0.210	0.190	8.63	16.22
103	Phenanthrene	Carbon Dioxide	45	0.210	0.180	10.40	10.43
104	Phenanthrene	Carbon Dioxide	45	0.180	0.150	5.62	8.80
105	Phenanthrene	Carbon Dioxide	50	0.180	0.310	7.38	11.86
106	Phenanthrene	Carbon Dioxide	55	0.410	0.310	37.99	33.65
107	Phenanthrene	Carbon Dioxide	55	0.160	0.150	2.89	11.63
108	Phenanthrene	Carbon Dioxide	65	0.140	0.120	6.01	8.84
109	Phenanthrene	Carbon Dioxide	70	0.160	0.150	13.52	15.42
110	Phenanthrene	Ethane	30	0.170	0.160	7.63	9.17
111	Phenanthrene	Ethane	40	0.130	0.130	3.62	7.90
112	Phenanthrene	Ethane	60	0.120	0.090	6.92	9.13
113	Phenanthrene	Ethylene	25	0.450	0.320	4.46	4.93

No.	Solute	Solvent	Temp.(°C)	k_{12}		AVERR	
				PT + vdW	PR + vdW	PT + vdW	PR + vdW
114	Phenanthrene	Ethylene	45	0.100	0.110	7.73	11.18
115	Phenanthrene	Ethylene	45	0.310	0.390	0.70	1.32
116	Phenanthrene	Ethylene	45	0.140	0.140	6.63	6.62
117	Phenanthrene	Ethylene	55	0.040	0.060	16.25	16.86
118	Phenanthrene	Ethylene	65	0.490	0.470	66.68	63.84
119	Phenanthrene	Ethylene	70	0.030	0.070	17.95	27.96
120	Phenanthrene	Ethylene	70	0.490	0.410	0.02	0.82
121	Triphenylmethane	Carbon Dioxide	30	0.740	0.480	9.20	28.35
122	Triphenylmethane	Carbon Dioxide	40	0.240	0.330	13.56	25.10
123	Triphenylmethane	Carbon Dioxide	50	0.200	0.160	10.50	11.67
124	Triphenylmethane	Ethylene	30	0.240	0.170	10.83	21.02
125	Triphenylmethane	Ethylene	40	0.210	0.150	10.42	20.34
126	Triphenylmethane	Ethylene	50	0.190	0.170	6.55	14.12

Table B-3. Comparison New Mixing Rule with Different Equations of State

No.	Solute	Solvent	Temp.(C)	k_{12}		AVERR	
				PT + NMR	PR + NMR	PT + NMR	PR + NMR
1	Acridine	Carbon Dioxide	35	0.03	1.29	14.378	8.69
2	Acridine	Carbon Dioxide	45	0.05	1.10	8.862	9.97
3	Acridine	Carbon Dioxide	55	0.07	0.05	21.051	27.49
4	Acridine	Carbon Dioxide	70	0.07	0.02	17.880	18.58
5	Acridine	Chlorotrifluoromethane	45	1.03	1.09	12.844	17.36
6	Acridine	Chlorotrifluoromethane	55	1.36	1.00	14.714	20.37
7	Acridine	Ethane	35	0.09	0.98	12.727	14.44
8	Acridine	Ethane	55	0.06	0.12	19.581	29.00
9	Acridine	Ethane	70	0.05	0.09	12.105	18.41
10	Acridine	Fluoroform	45	0.12	1.06	9.014	18.93
11	Acridine	Fluoroform	55	0.12	0.14	17.219	25.97
12	Anthracene	Carbon Dioxide	30	1.93	1.20	10.102	13.61
13	Anthracene	Carbon Dioxide	35	1.36	1.15	11.330	5.79
14	Anthracene	Carbon Dioxide	45	1.73	1.17	9.340	7.44
15	Anthracene	Carbon Dioxide	50	2.63	1.02	13.547	24.42
16	Anthracene	Carbon Dioxide	70	4.34	0.61	12.410	27.15
17	Anthracene	Ethane	30	2.53	0.95	10.468	34.28
18	Anthracene	Ethane	35	2.43	0.95	13.138	44.38
19	Anthracene	Ethane	50	3.05	0.82	8.128	45.03
20	Anthracene	Ethane	70	4.31	0.11	8.045	30.61
21	Anthracene	Ethylene	50	4.26	0.11	4.850	32.45
22	Anthracene	Ethylene	70	4.99	0.37	10.404	33.49
23	Anthracene	Ethylene	85	4.52	0.13	16.774	27.68
24	Benzoic Acid	Carbon Dioxide	45	-0.03	0.06	10.999	24.02
25	Benzoic Acid	Carbon Dioxide	55	-0.07	0.01	14.721	19.99
26	Benzoic Acid	Carbon Dioxide	65	-0.11	-0.04	12.043	17.30

No.	Solute	Solvent	Temp.(C)	k_{12}		AVERR	
				PT + NMR	PR + NMR	PT + NMR	PR + NMR
27	Benzoic Acid	Ethylene	45	-0.02	0.05	12.385	12.31
28	Benzoic Acid	Ethylene	55	-0.05	0.04	8.664	8.72
29	Benzoic Acid	Ethylene	65	-0.08	0.03	15.152	11.03
30	Fluorene	Carbon Dioxide	30	-0.06	0.85	23.822	35.10
31	Fluorene	Carbon Dioxide	35	-0.05	0.78	22.477	34.64
32	Fluorene	Carbon Dioxide	50	-0.04	-0.02	16.827	27.18
33	Fluorene	Carbon Dioxide	70	-0.05	-0.06	20.271	27.55
34	Fluorene	Ethylene	25	3.88	0.04	14.787	62.11
35	Fluorene	Ethylene	45	-0.06	-0.01	34.635	41.28
36	Fluorene	Ethylene	70	-0.10	-0.06	31.598	32.45
37	Hexamethylbenzene	Carbon Dioxide	30	1.21	0.41	21.080	37.69
38	Hexamethylbenzene	Carbon Dioxide	50	3.21	0.02	21.121	32.89
39	Hexamethylbenzene	Carbon Dioxide	70	-0.01	-0.04	29.952	34.82
40	Hexamethylbenzene	Ethylene	25	4.98	0.06	24.569	67.24
41	Hexamethylbenzene	Ethylene	45	-0.03	0.01	45.850	54.88
42	Hexamethylbenzene	Ethylene	70	-0.05	-0.03	34.343	37.27
43	Hexachloroethane	Carbon Dioxide	35	-0.07	0.01	25.555	45.68
44	Hexachloroethane	Carbon Dioxide	45	-0.12	-0.07	10.407	12.48
45	Hexachloroethane	Carbon Dioxide	55	-0.17	-0.12	40.294	38.86
46	2,3 - Dimethynaphthalene	Carbon Dioxide	45	-0.03	0.70	9.567	28.57
47	2,3 - Dimethynaphthalene	Carbon Dioxide	55	-0.04	0.03	8.398	16.16
48	2,3 - Dimethynaphthalene	Ethylene	35	-0.05	0.03	18.293	23.10
49	2,3 - Dimethynaphthalene	Ethylene	45	-0.08	0.00	15.465	16.64
50	2,3 - Dimethynaphthalene	Ethylene	55	-0.12	-0.02	15.519	21.31
51	2,6 - Dimethynaphthalene	Carbon Dioxide	35	-0.06	0.59	11.028	36.35
52	2,6 - Dimethynaphthalene	Carbon Dioxide	45	-0.05	0.03	1.659	9.99
53	2,6 - Dimethynaphthalene	Carbon Dioxide	55	-0.05	0.01	3.414	10.34
54	2,6 - Dimethynaphthalene	Ethylene	35	-0.08	0.00	17.418	21.87

No.	Solute	Solvent	Temp.(C)	k_{12}		AVERR	
				PT + NMR	PR + NMR	PT + NMR	PR + NMR
55	2,6 - Dimethynaphthalene	Ethylene	45	-0.11	-0.03	18.861	17.98
56	2,6 - Dimethynaphthalene	Ethylene	55	-0.17	-0.09	18.866	30.10
57	Naphthalene	Carbon Dioxide	35	4.89	0.20	18.466	34.93
58	Naphthalene	Carbon Dioxide	35	4.95	0.01	22.636	37.56
59	Naphthalene	Carbon Dioxide	36	4.96	0.17	19.274	27.99
60	Naphthalene	Carbon Dioxide	45	-0.10	-0.04	18.643	23.89
61	Naphthalene	Carbon Dioxide	45	-0.10	-0.04	22.120	28.38
62	Naphthalene	Carbon Dioxide	55	-0.15	-0.09	9.343	13.05
63	Naphthalene	Carbon Dioxide	55	-0.15	-0.09	12.348	16.54
64	Naphthalene	Carbon Dioxide	55	-0.15	-0.08	13.620	18.51
65	Naphthalene	Chlorotrifluoromethane	35	1.97	0.02	14.555	44.45
66	Naphthalene	Chlorotrifluoromethane	45	0.09	-0.04	22.928	18.19
67	Naphthalene	Chlorotrifluoromethane	55	0.04	-0.07	20.164	11.55
68	Naphthalene	Ethane	20	0.97	0.21	24.968	81.57
69	Naphthalene	Ethane	25	3.57	0.10	19.109	81.47
70	Naphthalene	Ethane	35	4.79	-0.08	24.690	79.07
71	Naphthalene	Ethane	35	4.90	-0.07	30.772	40.94
72	Naphthalene	Ethane	45	-0.06	-0.11	19.458	20.70
73	Naphthalene	Ethane	45	-0.08	-0.13	27.473	29.71
74	Naphthalene	Ethane	55	-0.17	-0.21	11.113	10.19
75	Naphthalene	Ethylene	12	-0.03	0.01	17.958	25.11
76	Naphthalene	Ethylene	12	4.85	0.00	16.130	45.01
77	Naphthalene	Ethylene	25	-0.07	-0.03	16.991	22.81
78	Naphthalene	Ethylene	25	-0.03	0.02	23.681	25.58
79	Naphthalene	Ethylene	25	-0.08	-0.05	21.648	25.26
80	Naphthalene	Ethylene	35	-0.12	-0.08	11.344	11.42
81	Naphthalene	Ethylene	35	-0.13	-0.09	17.712	19.77
82	Naphthalene	Ethylene	45	-0.19	-0.17	12.368	75.31

No.	Solute	Solvent	Temp.(C)	k_{12}		AVERR	
				PT + NMR	PR + NMR	PT + NMR	PR + NMR
83	Naphthalene	Ethylene	45	-0.17	-0.14	5.912	6.48
84	Naphthalene	Ethylene	45	-0.20	-0.15	12.660	12.51
85	Naphthalene	Ethylene	50	-0.27	-0.24	21.055	44.41
86	Naphthalene	Ethylene	50	-0.23	-0.18	7.421	5.11
87	Naphthalene	Ethylene	60	-0.39	-0.31	0.202	0.13
88	Naphthalene	Fluoroform	35	3.04	0.03	11.431	28.37
89	Naphthalene	Fluoroform	45	0.03	-0.01	19.813	18.82
90	Naphthalene	Fluoroform	55	-0.02	-0.04	13.314	11.10
91	1,4 - Naphthoquinone	Carbon Dioxide	45	-0.04	0.05	10.174	25.04
92	1,4 - Naphthoquinone	Carbon Dioxide	55	-0.05	0.02	9.367	17.25
93	1,4 - Naphthoquinone	Carbon Dioxide	70	-0.08	-0.02	11.212	13.64
94	1,4 - Naphthoquinone	Chlorotrifluoromethane	45	0.24	0.24	20.524	25.68
95	1,4 - Naphthoquinone	Chlorotrifluoromethane	55	0.19	0.20	14.903	16.67
96	1,4 - Naphthoquinone	Ethane	35	1.06	0.27	5.282	69.64
97	1,4 - Naphthoquinone	Ethane	45	0.14	0.19	20.959	33.29
98	1,4 - Naphthoquinone	Ethane	55	0.12	0.17	14.499	21.18
99	1,4 - Naphthoquinone	Ethane	70	0.07	0.13	17.005	18.98
100	1,4 - Naphthoquinone	Fluoroform	45	0.03	0.07	10.530	17.98
101	1,4 - Naphthoquinone	Fluoroform	55	-0.01	0.04	25.465	28.03
102	Phenanthrene	Carbon Dioxide	30	0.02	0.09	4.746	59.23
103	Phenanthrene	Carbon Dioxide	45	0.04	0.04	7.930	14.52
104	Phenanthrene	Carbon Dioxide	45	0.03	0.05	5.789	15.30
105	Phenanthrene	Carbon Dioxide	50	0.04	0.03	7.830	11.46
106	Phenanthrene	Carbon Dioxide	55	0.14	0.09	34.886	31.22
107	Phenanthrene	Carbon Dioxide	55	0.05	0.02	7.612	10.17
108	Phenanthrene	Carbon Dioxide	65	0.05	0.02	5.332	6.66
109	Phenanthrene	Carbon Dioxide	70	0.07	0.01	14.589	14.14
110	Phenanthrene	Ethane	30	0.05	0.18	23.611	69.20

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No.	Solute	Solvent	Temp.(C)	k_{12}		AVERR	
				PT + NMR	PR + NMR	PT + NMR	PR + NMR
111	Phenanthrene	Ethane	40	0.01	0.10	11.362	30.60
112	Phenanthrene	Ethane	60	0.01	0.08	10.151	17.36
113	Phenanthrene	Ethylene	25	0.33	0.38	5.429	6.73
114	Phenanthrene	Ethylene	45	0.04	0.06	14.538	16.64
115	Phenanthrene	Ethylene	45	0.32	0.40	1.849	2.22
116	Phenanthrene	Ethylene	45	0.04	0.11	15.927	24.92
117	Phenanthrene	Ethylene	55	0.01	0.02	17.773	26.27
118	Phenanthrene	Ethylene	65	1.34	0.11	55.006	69.70
119	Phenanthrene	Ethylene	70	0.01	0.03	10.993	27.58
120	Phenanthrene	Ethylene	70	0.34	0.30	0.286	0.22
121	Triphenylmethane	Carbon Dioxide	30	0.28	-0.11	8.575	31.44
122	Triphenylmethane	Carbon Dioxide	40	0.03	-0.10	8.040	10.98
123	Triphenylmethane	Carbon Dioxide	50	0.04	-0.10	12.927	12.59
124	Triphenylmethane	Ethylene	30	0.09	-0.02	14.367	13.76
125	Triphenylmethane	Ethylene	40	2.36	0.01	7.195	15.06
126	Triphenylmethane	Ethylene	50	2.96	-0.03	9.472	10.74

APPENDIX C. MATLAB PROGRAMS

An algorithm was developed in Matlab to predict the solubility of solids in supercritical fluids based on the selected equation of state (EoS) and mixing rules. Also, the best EoS parameters were found by comparing the experimental (from the database) and predicted solubilities, using an objective function that was minimized. To appreciate the quality of the predictions, the percent average error was calculated for each of thermodynamic models. The program has the following steps:

1. Read the properties of the solvent and the solute and the solubility data for the isotherm of the system used.

2. Calculate the parameters of the components of the system, according to the equation of state.

3. To calculate the solubility of the solid in the supercritical fluid, a series of equations was developed, using the mixing rules to calculate the mixture parameters. An interaction parameter that minimizes the percent error is then sought. This is done by the program and is also shown graphically.
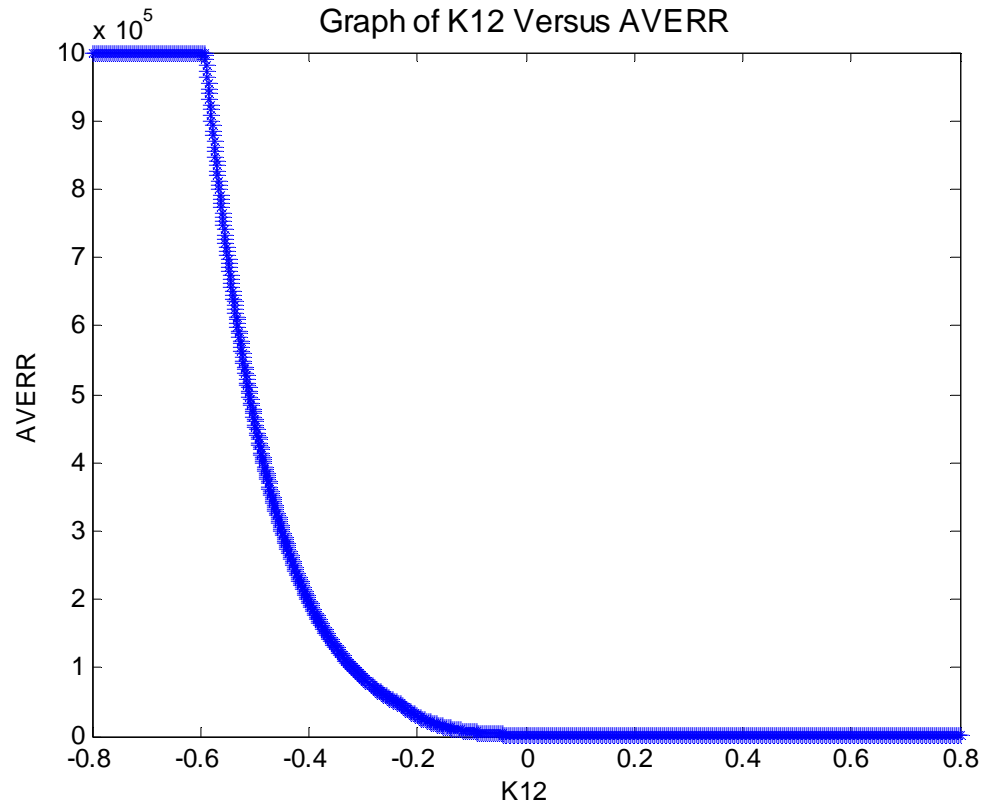
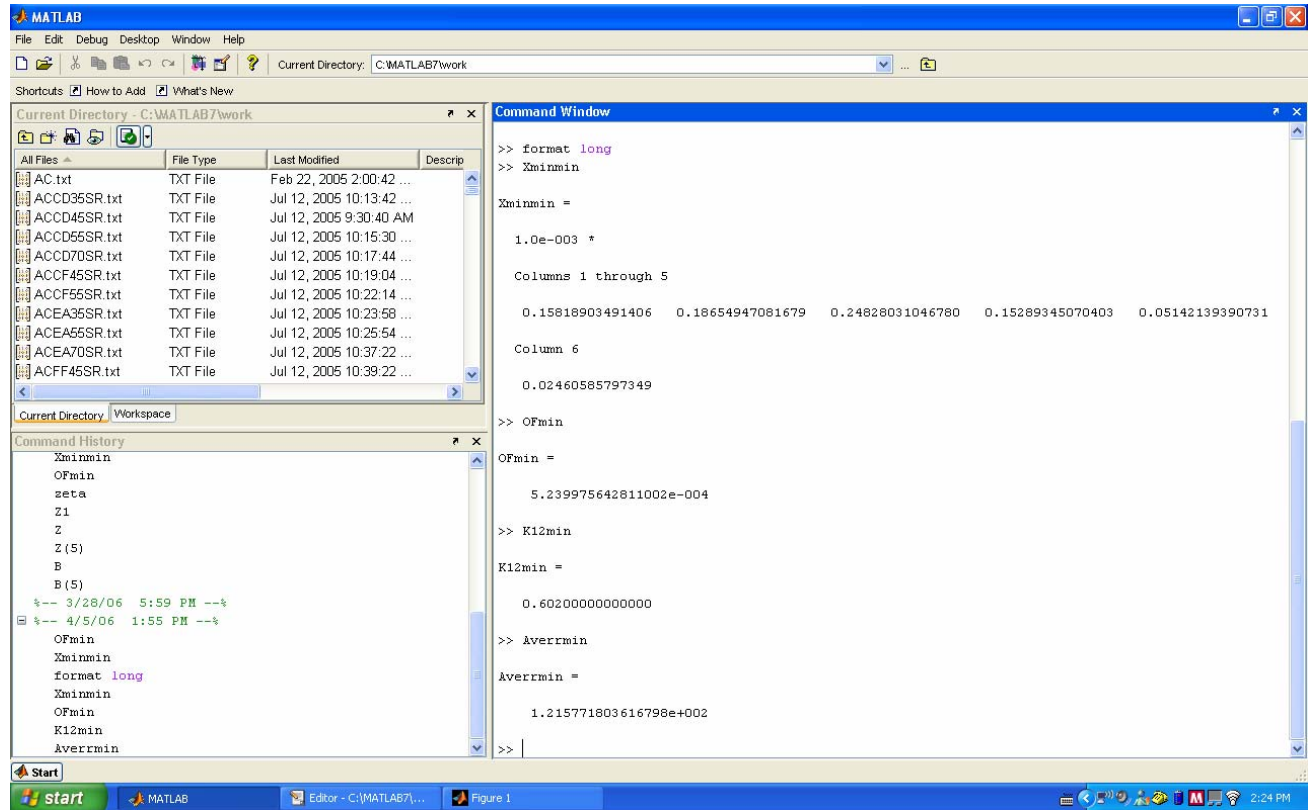**Figure C-1. Graph of** AVERR **versus** k_{12}

Figure C-2. Parameters of program in Matlab

The parts of the program are:

1. Data of Solvent:

```
load FF.txt;
FF;
disp('Presión Crítica del Solvente en Pa:')
Pc1 = FF(1,1);
disp('Temperatura Crítica del Solvente en Grados Kelvin:')
Tc1 = FF(2,1);
disp('Factor Acentrico del Solvente:')
W1 = FF(3,1);
disp('Peso Molecular del Solvente en gramos por mol:')
PM1 = FF(4,1);
```

2. Data of Solute:

```
load AC.txt;
AC;
disp('Presión Crítica del Soluto en Pa:')
```

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```
Pc2 = AC(1,1);
disp('Temperatura Crítica del Soluto en Grados Kelvin:')
Tc2 = AC(2,1);
disp('Factor Acentrico del Soluto:')
W2 = AC(3,1);
disp('Volumen Molar del Soluto en m^3 por gmol:')
VM2 = AC(4,1);
disp('Constantes de Antoine del Soluto:')
An = AC(5,1);
Bn = AC(6,1);
disp('Peso Molecular del Soluto en gramos por mol:')
PM2 = AC(7,1);
```

3. Solubility Data of System:

```
load ACFF45SR.txt
ACFF45SR;
disp('Numero de Datos Experimentales:')
N = ACFF45SR(1,1);
disp('Temperatura del Sistema en Grados Kelvin:')
T = ACFF45SR(1,2);
disp('Valores Experimentales de Presion en Pa y de Solubilidad:')
Exp = ACFF45SR(2:N+1,:);
P = ACFF45SR(2:N+1,1);
Yexp = ACFF45SR(2:N+1,2);
```

4. Critical and Reduced Temperature and Pressure and Acentric Factor:

```
Tc = [Tc1; Tc2];
Tr = T./Tc;
Pr = P/Pc1;
Pc = [Pc1; Pc2];
W = [W1; W2];
```

5. Parameters of Peng-Robinson EoS for pure components:

```
ac = (0.45724 *(((Tc.^2)*R^2)./Pc));
b = 0.07780 * ((R*Tc)./Pc);
m = (0.37464 + 1.54226*W - 0.26992*W.^2);
alpha = (1 + m.*(1 - Tr.^0.5)).^2;
a = ac .* alpha;
```

6. Sublimation (vapor) Pressure of the solute:

```
P2sat = exp(An - (Bn/T));
```

7. Mixing Rule: Ranges of k_{12} and y_2, calculation of fugacity coefficient and compressibility factor:

```
for K12=-0.8:0.001:0.8
    cont = cont + 1;
```

```
K12g(cont)=K12;
conta=0;
i = 1;
   for X2n=0:0.01:0.1
     conta=conta+1;
       for r=1:N
          X1n(r) = 1-X2n;
          alp = a(2,1)/a(1,1);
          C1 = (56.4 + 2.41*alp - 66.5*Tr(1,1))^-2;
          C2 = (0.263 - 0.00534*alp + 0.0097*Tr(1,1))^0.5;
          e(r) = C1 + C2*(1/Pr(r));
          a12(r) = a(1,1) + e(r)*(a(2,1) - a(1,1))*(1-K12);
          amix(r) = a(1,1)*X1n(r)^2 + a(2,1)*X2n^2 + 2*a12(r)*X1n(r)*X2n;
          b12 = (sum(b) / 2)*(1-L12);
          bmix(r) = b(1,1)'*X1n(r)^2 + b(2,1)*X2n^2 + 2*b12*X1n(r)*X2n;
          A(r) = amix(r)*P(r)/(R*T)^2;
          B(r) = bmix(r)*P(r)/(R*T);
          Z1a(r) =  -(1-B(r));
          Z1b(r) = (A(r)-3*B(r)^2-2*B(r));
          Z1c(r) =  -(A(r)*B(r)-B(r)^2-B(r)^3);
          zeta = [1 Z1a(r) Z1b(r) Z1c(r)];
          F =[];
          G = [];
          G = roots(zeta);
          F = [F G];
             for l=1:3
                if imag(G(l))==0;
                PP(l) = G(l);
                end
              end
          Z(r) = max(PP);
        end
    Z1=Z';
    A1=A';
    B1=B';
    X1nn = X1n';
    X2n = (ones (N,1))*X2n;
    bmix1=bmix';
    amix1 = amix';
    fhi = exp((b(2,1)./bmix1).*(Z1-1)- log (Z1-B1)-
    (((A1./(2*sqrt(2).*B1)).*((2*((a12.*X1nn'+a(2,1).*X2n')./amix1')'-
    (b(2,1)./bmix1))).*log((Z1+(1+sqrt(2)).*B1)./(Z1+(1-sqrt(2)).*B1))));
    X2new = (P2sat./(P.*fhi)).*exp(VM2*(P./(R*T)));
    M = X2new;
    E = (M - Yexp).^2 ;
    OF = sqrt (sum(E)/N);
    W = sum (Yexp);
    AVERR = (100 * ((N*OF)/W));
    DIF1 = (abs(M - X2n)).^2;
    DIF = sum (DIF1);
    K12E(i)=K12;
    Rh(i)=OF;
    AVERRP (i) = AVERR;
    POSIC{i}=X2new;
```

```
        [v,p]=sort(AVERRP);
        jk =  p(1,1);
        [s,h]= size(p);
        K12EM = K12E(1,jk);
        AVERRM = AVERRP (1,jk);
        OFM = Rh(1,jk);
        i = i+1;
     end
    AVERRP2P=1000000;
    POSICI=zeros(N,1);
  for j=1:conta
    if AVERRP2P>AVERRP(j)
        AVERRP2P=AVERRP(j);
        POSICI=POSIC{j};
    end
  end

  AVERRP2(cont)=AVERRP2P;
  XMIN{cont}=POSICI;
  K12mi(cont)=K12;
end
%end
% Averrmin=min(AVERRP2)
Averrmin=10000;
Xminmin=zeros(6,1);
for j=1:cont
  if Averrmin>AVERRP2(j)
    Averrmin=AVERRP2(j);
    Xminmin=XMIN{j}';
    K12min=K12mi(j);
    R = (Xminmin - Yexp').^2 ;
    OFmin = sqrt (sum(R)/N);
  end
end
%end

figure(1);
plot(K12g,AVERRP2,'*');
xlabel('K12')
ylabel('AVERR')
title('Graph of K12 Versus AVERR','FontSize',12)
```