# Thermodynamic Equilibria Modeling of Ternary Systems of Solid Organics in Compressed Carbon Dioxide

Yousef Bakhbakhi

Department of Chemical Engineering, King Saud University,

P.O. Box 800, Riyadh, 11421, Saudi Arabia. ybakhbak@ksu.edu.sa

Carbon dioxide as a compressed gas is a non-polar molecule, thus it is not a particularly good solvent for polar organic compounds. Therefore, a polar cosolvent is usually recommended for enhancing the solubility power of compressed gas for polar organic compounds. Moreover, accurate prediction of compressed gas behavior in mixtures is highly required, besides the experimental assessments of the influence of key operating parameters. 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 Stryjek and Vera modified Peng-Robinson equation of state (PRSV EoS) 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 different ternary systems for which experimental data were available; 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.

## 1. Introduction

The recent increase in the use of supercritical fluids for separation processes requires the knowledge of theoretical interpretations and predictions of phase behavior of supercritical fluids in multicomponent systems. Moreover, in order to design and to scale a supercritical fluid based process up to the industrial level, it is of paramount importance to get a detailed understanding of all the phenomena involved. Good understanding of the phase behavior of supercritical fluids with various compounds become necessary for efficient design of such production systems. The investigated influence of polar cosolvents on the solubility of polar solids in supercritical carbon dioxide showed that the addition of a small amount of a polar cosolvent could significantly increase the solvating power of supercritical $CO_2$. Nonetheless, 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) ( Cháfer et al., 2004), solutions theories (Li et al., 2004), expanded liquid model (Brogle, 1982), cluster solvation model (Cheng et al., 2003), and density-based model (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), proposed 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. Cháfer *et al.*, 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. The first model combines the Carnahan–Starling repulsive-type equation for hard spheres, with a group contribution version of a density-dependent NRTL-type expression to evaluate attractive interactions between molecules. The second model is a well known, and widely used representative of the cubic equations from van der Waals EoS family. Moreover, Huang *et al.*, (2004) used the Peng-Robinson (PR) EoS and the empirical density-based models of Chrastil and Kumar and Johnston to correlate the solubility data of cholesterol and cholesteryl benzoate in supercritical $CO_2$ in the presence of the polar cosolvents methanol and acetone. Their results concluded that although the density-based models provided a better correlation of the experimental data with a far lower value of average absolute relative deviation (AARD) than the PR EoS, the latter 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. Furthermore, cubic equations of state are proved to be highly successful for phase equilibrium calculations of multicomponent systems. In this investigation, the PRSV approach was employed for modeling the solubility of anthracene in supercritical carbon dioxide with and without cosolvents.

## 2. Mathematical Framework

As stated above, the limitation of experimental data dealing with supercritical fluids mixtures and since these mixtures deal with high-pressure phase equilibria, there is considerable interest in mathematical models that can accurately predict the phase behavior of such systems. The equation of state (EoS) method is considered to be the most suitable approach for modeling such kind of systems. Although many investigations have been carried out for modeling the solubility of solids in supercritical fluid mixtures, the modeling of the solubility of solids in supercritical fluids with cosolvents are much less, and cubic EoSs are commonly used. The Stryjek and Vera modified Peng-Robinson equation of state, the so-called PRSV has received great attention since its publication. In this work, the PRSV approach is further applied to model the solubility of solute solid in supercritical fluid with cosolvent mixture. The volumetric expansion of the liquid phase is simulated using the Stryjek and Vera modified Peng-Robinson equation of state (PRSV) EoS.

The Peng-Robinson equation of state is given by:

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + 2v\,b - b^2} \tag{1}$$

The solubility of the solid $i$ in a supercritical fluid and cosolvent is determined by the following equation:

$$y_i = \left(P_i^{sat} \middle/ P\phi_i\right)\exp\left(V_i^{sol} P \middle/ RT\right) \qquad (2)$$
(16)

where $P_i^{sat}$, $V_i^{sol}$, and $\phi_i$ are the sublimation pressure, solid molar volume, and the fugacity coefficient of component $(i)$ in either the liquid or vapor phase.

The optimization procedure is based on the minimization of the error between the calculated and experimental values. The expression for the objective function is:

$$\min OF(p) = \left(\frac{1}{n}\sum_{i=1}^{n}(dist(y_i(p)-m_i))^2\right)^{1/2}; \quad p \in R^n \qquad (3)$$

## 3. Results and Discussion

The values for the experimental solubilities of anthracene in supercritical carbon dioxide with cosolvents, acetone, ethanol and cyclohexane were taken from literature (Bae *et al.*, 2004, Cháfer *et al.*, 2004). Figs. 1 and 2 show the solubility behavior at temperatures, 318.1 K and 328.1 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 ethanol and cyclohexane, all at 4 mole %. It is obvious that the calculated interaction parameters yield good agreement between the calculated and experimental solubility data. The best agreement was obtained with the experimental solubility data of acetone as a cosolvent. However, errors can occur in the solubility measurements and also in the thermal analysis using DSC. An error of ±10% in measuring the heat of fusion, and thus heat capacity and melting point, can result in a deviation up to 80% in the solubility prediction. Figs. 3 and 4 show the effect of temperature on the solubility for the systems anthracene- $CO_2$- acetone, anthracene- $CO_2$- ethanol, and anthracene- $CO_2$- cyclohexane using the calculated solubility data with the PRSV EoS and the calculated interaction parameters. It is clear that the addition of a cosolvent can have a dramatic effect on the supercritical fluids phase behavior and on the solubility of the solute. 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. Figs. 3 and 4 show the effect of temperature on the solubility for the systems anthracene- $CO_2$- acetone, anthracene- $CO_2$- ethanol, and anthracene- $CO_2$- cyclohexane using the calculated solubility data with the PRSV EoS and the calculated interaction parameters. It is clear that the addition of a cosolvent can have a dramatic effect on the supercritical fluids phase behavior and on the solubility of the solute. 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. 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.
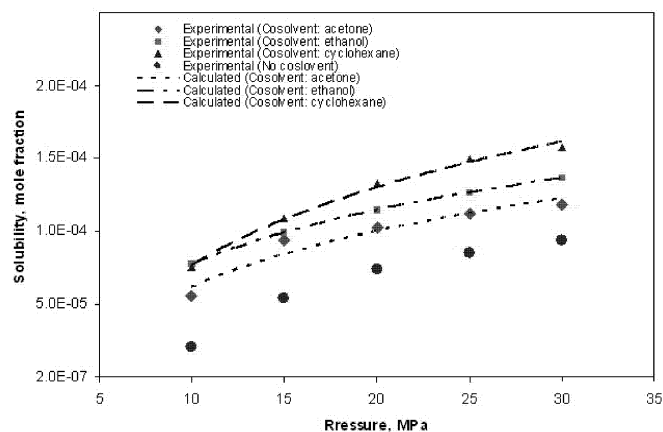
**Figure 1.** *Behavior of the system anthracene-$CO_2$ and the cosolvents, acetone, ethanol, and cyclohexane at 318.1 K. The data points {, ▲,■,◆,●}are experimental values whereas the lines are EoS predicted data.*

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. Ting *et al.* (1993), indicated that the use of a polar cosolvent for polar solutes, may cause the largest increase in solubility as a result of some specific chemical interactions like hydrogen bonding or charge transfer complex formation. The temperature has an effect on the solubility of the solute in $CO_2$.
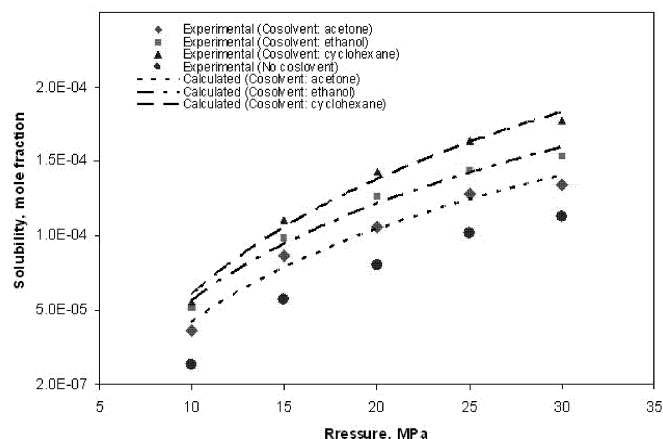


**Figure 2.** *Behavior of the system anthracene-$CO_2$ and the cosolvents, acetone, ethanol, and cyclohexane at 328.1 K. The data points {, ▲,■,◆,●}are experimental values whereas the lines are EoS predicted data.*
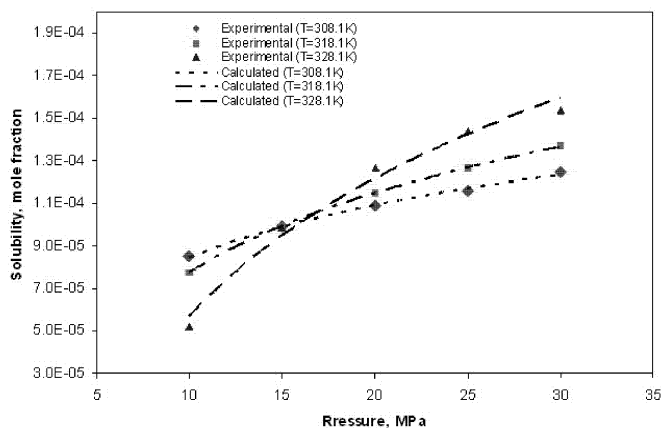
**Figure 3.** *Behavior of the system anthracene-$CO_2$-ethanol at 308.1 K, 318.1 K, and 328.1 K . The data points {, ▲,■,♦}are experimental values whereas the lines are EoS predicted data.*

For the system studied in this work, it was observed that at low pressures, 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 Figs. 1 and 2 for the system anthracene- $CO_2$-acetone at temperatures of 318.1 K and 328.1 K where the highest solubilities were obtained at the highest temperature and pressures above approximately 15 MPa. Chimowitz and Pennisi (1986), explained that the solubility enhancement at high pressures and temperatures may be caused by the fact that at pressures below the crossover pressure, the density of the gas is more sensitive to temperature changes than at higher pressures. At higher pressures, above the crossover point, the vapor-pressure effect is more important than the density effect.
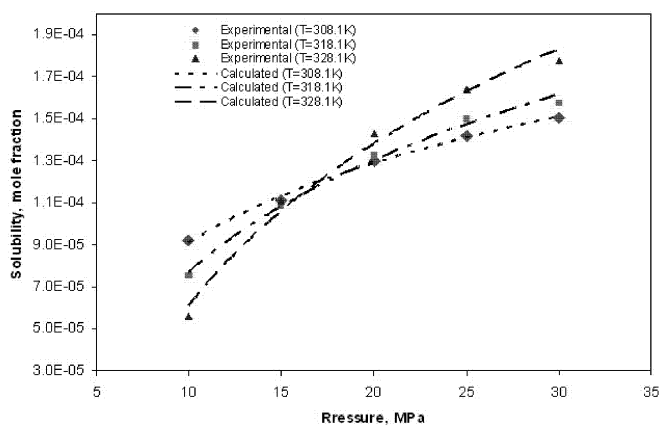


**Figure 4.** *Behavior of the system anthracene-$CO_2$-cyclohexane at 308.1 K, 318.1 K, and 328.1 K . The data points {, ▲,■,♦}are experimental values whereas the lines are EoS predicted data.*

## 4. Conclusions

In this investigated thermodynamic equilibria, the Stryjek and Vera modified Peng-Robinson equation of state (PRSV) EoS and the VDW mixing rules model were used to determine solubilities of systems that involved solid, supercritical fluid, and cosolvent. The solubility of the systems anthracene- $CO_2$- acetone, anthracene- $CO_2$- ethanol, and anthracene- $CO_2$- cyclohexane was influenced by the pressure and temperature. The best agreement was obtained with the experimental solubility data of acetone as a cosolvent although the solubility of anthracene, was higher with the non-polar cosolvent cyclohexane than with the polar cosolvents ethanol and acetone.

### Acknowledgments

## References

Bae H., Jeon J., and Lee. H., 2004, Influence of Co-solvent on Dye Solubility in Supercritical Carbon Dioxide. *Fluid Phase Equilibria*, 222-223, 119-125.

Brogle H., 1982, $CO_2$ as a solvent: its properties and applications. *Chemistry and Industry*, 385-390.

Chafer A., Fornari T., Berna A., and Stateva R.P., 2004, Solubility of Quercetin in Supercritical CO2 + Ethanol as a Modifier: Measurements and Thermodynamic Modelling. *The Journal of Supercritical Fluids*, 32, 89-96.

Cheng K., Tang M., and Chen Y., 2003, Calculations of Solid Solubility in Supercritical Fluids using a Simplified Cluster Solvation Model. *Fluid Phase Equilibria*, 214, 169-186.

Chimowitz E.H. and Pennisi. K.J., 1986, Process Synthesis Concepts for Supercritical Gas Extraction in the Crossover Region. *AIChE Journal*, 32, 1665-1676.

Guha S. and Madras G., 2001, Modeling of Ternary Solubilities of Organics in Supercritical Carbon Dioxide. *Fluid Phase Equilibria*, 4736, 1-10.

Huang Z., Kawi S., and Chiew Y.C., 2004, Solubility of Aspirin in Supercritical Carbon Dioxide with and without Acetone. *J. Chem. Eng. Data*, 49, 1323-1327, 2004.

Jin J., Zhong C., Zhang Z., and Li Y., 2004, Solubilities of Benzoic Acid in Supercritical CO2 with Mixed Co-Solvent. *Fluid Phase Equilibria*, 226, 9-13.

Li Q., Zhong C., Zhang Z., and Zhou Q. , 2004, Modeling of the Solubility of Solid Solutes in Supercritical CO2 with and without Cosolvent using Solution Theory. *Korean J. Chem. Eng.*, 21, 1173-1177.

Peng D. and Robinson D.B. , 1976, A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.*, 15, 59-64.

Stryjek R., Vera J. H., 1986, PRSV: an improved Peng–Robinson equation of state for pure compounds and mixtures, *Can. J. Chem. Eng.* 64,323.

Ting S.S.T., Macnaughton S.J., Tomasko D.L., and Foster N.R., 1993, Solubility of Naproxen in Supercritical Carbon Dioxide with and without Cosolvents. *Ind. Eng. Chem. Res.*, 32, 1471- 1481.