SHORT COMMUNICATION

A comparison among three equations of state in predicting the solubility of some solids in supercritical carbon dioxide

Mohammad Reza Housaindokht*,†, Behzad Haghighi and **Mohammad Reza Bozorgmehr*,****

*Biophysical Chemistry Laboratory, Department of Chemistry, Faculty of Science, Ferdowsi University, Mashhad, Iran
**Thermophysical Properties Research Laboratory (TPRL), Department of Chemistry,
Faculty of Science, Birjand University, Birjand, Iran
***Department of Chemistry, Faculty of Science, Islamic Azad University, Mashhad, Iran

Abstract–Equations of state play an important role in chemical engineering designs, and they have assumed an expanding role in the study of the phase equilibria of fluids and fluid mixtures. In this report, a modified Peng-Robinson equation of state by Danesh et al., a modified Peng-Robinson equation of state by Gasem et al., and the Mansoori-Mohsen Nia-Modarress equation of state are used to predict the solubility of some solids in supercritical carbon dioxide. The systems studied were binary mixtures containing supercritical carbon dioxide with Ascorbic acid, Ascorbyl palmitate, Butyl hydroxyl anisole, Dodecyl gallate and Propyl gallate. Interaction parameters for the studied systems are obtained and the percentage of average absolute relative deviation (%AARD) in each calculation is displayed.

Key words: Equation of State, Solid Solubility, Supercritical Carbon Dioxide

INTRODUCTION

The need to understand the fundamentals of supercritical fluid processing and the application of this technique to an increasingly wide range of materials and conditions continues to grow. Carbon dioxide as a supercritical fluid has many excellent properties such as non-toxicity, non-explosiveness, ready availability and ease of removal from the extracted products. In the last few decades, the solubilities of different solutes in supercritical fluids have been measured extensively [Choi et al., 1996, 1997; Chang et al., 1996; Noh et al., 1995; Hong et al., 1990].

Since solubility data of solids and their mixtures in supercritical fluid are limited and the accurate measurement of the solid solubility in supercritical fluid is also difficult and time consuming, there is thus considerable interest in mathematical models that can accurately predict the phase behavior of such systems. Equations of state in combination with mixing rules are currently the most widely models used for the calculation of solubility of components in supercritical fluids [Skerget et al., 2002]. Some of the works done in this area are [Neau et al., 2005; Lee et al., 2005; Yener et al., 2005].

In this study a modified Peng-Robinson equation of state by [Danesh et al., 1995] (MPR1), a modified Peng-Robinson equation of state by [Gasem et al., 2001] (MPR2) and The Mansoori-Mohsen-Nia-Modarress equation of state [Mansoori et al., 2003] (MMM) are used to predict the solubility of Ascorbic acid, Ascorbyl palmitate, Butyl hydroxyl anisole, Dodecyl gallate and Propyl gallate. Interaction parameters for the studied systems are obtained and the percentage of average absolute relative deviation (%AARD) in each calculation is displayed.

METHODOLOGY

The method for modeling equilibrium data involved calculating the fugacity of the components in the different phases and making them equal. In this way, the solubility of the solid solute in the supercritical fluid can be calculated by means of Eq. (1), which considers a solid phase composed of the pure solute in equilibrium with a fluid phase formed by a mixture of solvent and solute.

$$y = \frac{P^{sub} \exp\left[V_S\left(\frac{P - P^{sub}}{RT}\right)\right]}{\phi^{SCF}P} \tag{1}$$

In the derivation of this equation, it is assumed that the supercritical solvent does not dissolve in the condensed phase, the solid state is incompressible, condensed phase vapor pressure is very low and its molar volume is independent of pressure. In Eq. (1) ϕ^{SCF} is the fugacity coefficient of solute in supercritical phase and can be calculated by using an equation of state by the thermodynamic relationship (Appendix 1). Equations of state and Van der Waals mixing rule used in this study are given in Appendix 1.

The binary interaction parameter k_{12} at a given temperature is obtained by regressing the model against experimental solubility data. The fitness function at each temperature is the percentage average absolute relative deviation (%AARD) between the calculated and experimental solubility:

$$\%AARD = \frac{100}{N}\sum_i^N \frac{|y_{exp} - y_{calc}|}{y_{exp}} \tag{2}$$

where N is the number of experimental data. Values of required physical properties of all compounds used are displayed in Table 1.

RESULTS AND DISCUSSION

Experimental data on the solubility of solids in carbon dioxide were taken from the [Cortesi et al., 1999]. Average absolute relative deviation for different CO$_2$-solutes systems is shown in Table 2.

---

†To whom correspondence should be addressed.
E-mail: mr_housaindokht@yahoo.com

Table 1. Required physical properties of all compound used [Cortesi et al., 1999]

Compound	T_C (K)	P_C (bar)	ω	$V_{S(cm^3/mol)}$	P^{sub} (bar, T=313.15 K)
Carbon dioxide	304.2	73.76	0.225		
Ascorbic acid	790.91	44.19	1.57	106.7	6.2E-06
Ascorbyl palmitate	870.81	11.56	1.85	340.50	1.14E-14
Butyl hydroxyl anisole	798.78	28.83	0.63	168.8	1.1E-05
Dodecyl gallate	905.90	18.46	1.20	267.9	2.0E-11
Propyl gallate	862.87	47.72	0.86	155.0	2.5E-08

Table 2. %AARD value for various components used in this study

Component	EOS		
	MPR1	MPR2	MMM
Ascorbic acid	10.95133	11.57724	10.88523
Ascorbyl palmitate	26.63833	29.71215	75.16237
Butyl hydroxyl anisole	8.69860	7.37967	9.85055
Dodecyl gallate	5.41113	5.37072	5.04757
Propyl gallate	6.86714	6.03261	8.92317

Table 3. Regressed interaction parameters between CO₂ and solute (T=313.15)

Compound	k12		
	MPR1	MPR2	MMM
Ascorbic acid	0.5131	0.4597	0.2168
Ascorbyl palmitate	0.2621	0.1683	−0.0010
Butyl hydroxyl anisole	0.1225	0.0704	−0.0488
Dodecyl gallate	0.2910	0.2224	−0.0520
Propyl gallate	0.2983	0.2460	0.0924

It should be pointed out that the MMM equation is a two-constant parameter equation of state, while the MPR1 and MPR2 are three-constant parameter equations. In applying equations of state to calculate the solubility of solutes in supercritical solvents, data for the critical properties, i.e., the critical temperature and pressure, of the compound involved are needed. For three-parameter equations of state, a third parameter is needed; the MPR1 and MPR2 equations of state need the data of acentric factor. Values of required physical properties of all compounds used are listed in Table 1.

Average absolute relative deviations for Ascorbic acid in supercritical carbon dioxide, predicted by MPR1, MPR2 and MMM equations of state, are shown in Table 2. According to this table, the value of %AARD for the MMM equation of state is less than for those of MPR1 and MPR2.

Average absolute relative deviations for the Ascorbyl palmitate in supercritical carbon dioxide, predicted by MPR1, MPR2 and MMM equations of state, are shown in Table 2. According to this table, the MPR1 equation of state has less %AARD than MPR2 and MMM. The high value of %AARD for the MMM equation of state is accounted for by two factors: first, inaccuracy of physical properties of pure components such as critical properties and molar volume, for example, at 40 MPa and 310 K, an 11% error in the solid molar volume of naphthalene would correspond to a 21% error in extraction percentage [Ashour et al., 2000]; and second, the high asymmetry in size of Ascorbyl palmitate and carbon dioxide.

Average absolute relative deviations for the Butyl hydroxyl anisole in supercritical carbon dioxide, predicted by MPR1, MPR2 and MMM equations of state, are shown in Table 2. According to this table, the MPR2 equation of state has less %AARD than MPR1 and MMM.

Average absolute relative deviations for the Dodecyl gallate in supercritical carbon dioxide, predicted by MPR1, MPR2 and MMM equations of state, are shown in Table 2. According to this table, the MMM equation of state has less %AARD than MPR1 and MPR2.

Average absolute relative deviation for the Propyl gallate in supercritical carbon dioxide, predicted by MPR1, MPR2 and MMM

equations of state, is shown in Table 2. According to this table, the MPR2 equation of state has less %AARD than MPR1 and MMM.

Interaction parameters for the studied systems are shown in Table 3.

CONCLUSION

Three equations of state, MPR1, MPR2 and MMM, are used to predict the solubility of some solids in supercritical carbon dioxide. According to the results, the overall %AARD value predicted by MMM equation of state is more than %AARD values for MPR1 and MPR2 equations of state. Also, in the case of Ascorbyl palmitate, as a large asymmetric component, %AARD value predicted by MMM equation of state has shown large deviation, indicating that the two parameter equation of state, MMM, is deficient in this situation.

APPENDIX 1

Equations of state and mixing rule used in this study are as follows:

PR EOS:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + 2bV - b^2} \qquad (3)$$

where

$$a = a_C \alpha(T) \qquad (4)$$

$$a_C = 0.45724 \frac{R^2 T_C^2}{P_C} \qquad (5)$$

$$b = 0.0778 \frac{R T_C}{P_C} \qquad (6)$$

Alpha functions for MPR1 and MPR2 EOS are:

$$\alpha(T_r) = [1 + 1.21*(0.3796 + 1.485\omega$$
$$- 0.1644\omega^2 + 0.01667\omega^3)(1 - \sqrt{T_r})]^2 \qquad (7)$$

$$\alpha(T_r) = T_r^{-0.792615}\exp(0.401219(1-T_r^{-0.99262}))$$

$$+ \omega\left(\begin{array}{c} T_r^{-1.98471}\exp(0.02496(1-T_r^{-9.98471})) \\ -T_r^{-0.792615}\exp(0.401219(1-T_r^{-0.99262})) \end{array}\right) \qquad (8)$$

MMM EOS:

$$P = \frac{RT(V+1.3191b)}{V(V-b)} - \frac{a}{T^{0.5}V(V+b)} \qquad (9)$$

$$a_C = 0.48748\frac{R^2T_C^{2.5}}{P_C} \qquad (10)$$

$$b = 0.06446\frac{RT_C}{P_C} \qquad (11)$$

For MPR1 and MPR2 the van der Waals mixing rule used:

$$a_m = \sum_i\sum_j y_iy_j\sqrt{a_ia_j}(1-k_{ij}) \qquad (12)$$

$$b_m = \sum_i y_ib_i \qquad (13)$$

for MMM EOS:

$$a_m = \sum_i\sum_j y_iy_j\sqrt{a_ia_j}(1-k_{ij}) \qquad (14)$$

$$b_m = \left(\frac{1}{4}\right)(3\sum_i\sum_j y_iy_jb_{ij} + \sum_i y_ib_{ii}) \qquad (15)$$

where k_{ij} is the interaction parameter.

The fugacity coefficient of component in a mixture derived from MPR1 and MPR2 equations of state is:

$$\ln\phi_i = \left[\frac{\partial(nb_m)/\partial n_i}{V-b_m} - \ln(V-b_m/V)\right] - \ln Z$$

$$- \frac{a_m}{b_mRT}\left[\frac{V}{(V+(1+\sqrt{2})b_m)(V+(1-\sqrt{2})b_m)}\right]\frac{\partial(nb_m)}{\partial n_i}$$

$$- \frac{a_m}{2\sqrt{2}RTb_m}\left\{\frac{1}{a_m}\left[\frac{1}{n}\frac{\partial(n^2a_m)}{\partial n_i}\right] - \frac{1}{b}\frac{\partial(nb_m)}{\partial n_i}\right\}\ln\left(\frac{(V+(1+\sqrt{2})b_m)}{(V+(1-\sqrt{2})b_m)}\right) \qquad (16)$$

Where

$$\frac{1}{n}\frac{\partial(n^2a_m)}{\partial n_i} = 2\sum_j y_j\sqrt{a_ia_j}(a-k_{ij}) \qquad (17)$$

$$\frac{\partial(nb_m)}{\partial n_i} = b_{ii} \qquad (18)$$

for MMM EOS:

$$\ln\phi_i = \left\{\begin{array}{c} 2.3191\left[\dfrac{3(2\sum_j y_jb_{ij} - \sum_i\sum_j y_iy_jb_{ij}) - b_{ii}}{4(V-b_m)} - \ln\left(1-\dfrac{b_m}{V}\right)\right] \\ -\ln Z + \dfrac{a_m}{RT^{1.5}\sum_i y_ib_{ii}} \\ \left[\left(\dfrac{b_{ii}}{\sum_i y_ib_{ii}} - \dfrac{2\sum_j y_ja_{ij}}{a_m}\right)\ln\left(1+\dfrac{\sum_i y_ib_{ii}}{V}\right) - \dfrac{b_{ii}}{V+\sum_i y_ib_{ii}}\right] \end{array}\right\} \qquad (19)$$

NOMENCLATURE

Abbreviations
EOS : equation n of state
MPR : modified Peng-Robinson
MMM : Mansoori-Mohsen-Nia-Modarress

Symbols
a   : equation of state parameter
b   : equation of state parameter
k_{ij} : interaction parameter
m   : equation of state parameter
P   : absolute pressure
R   : universal gas constant
T   : absolute temperature
V   : volume
Y   : mole fraction
Z   : compressibility factor

Greek Letters
α : equation of state parameter
ω : acentric factor

Subscripts
C   : critical state variable
r   : reduced state variable
i   : denote component i

REFERENCES

Ashour, I., Almehaideb, R., Fateen, S.-E. and Aly, G., "Representation of solid-supercritical fluid phase equilibria using cubic equations of state," *Fluid Phase Equilibria*, **167**, 41 (2000).

Chang, K. H., Bae, H. K. and Shim, J. J., "Dyeing of pet textile fibers and films in supercritical carbon dioxide," *Korean J. Chem. Eng.*, **13**, 310 (1996).

Choi, E. S., Shin, H. Y., You, S.-S. and Yoo, K.-P., "Measurement and correlation of solubilities of *o*-, *m*- and *p*-coumaric acid isomers in supercritical carbon dioxide," *Korean J. Chem. Eng.*, **14**, 292 (1997).

Choi, Y. H., Kim, J., Noh, M. J., Park, E. M. and Yoo, K.-P., "Extraction of epicuticular wax and nonacosan-10-ol from ephedra herb utilizing supercritical carbon dioxide," *Korean J. Chem. Eng.*, **13**, 216 (1996).

Christophe Nicolas, Evelyne Neau, Sofiane Meradji and Isabelle Raspo, "The Sanchez-Lacombe lattice fluid model for the modeling of solids in supercritical fluids," *Fluid Phase Equilibria*, **232**, 219 (2005).

Cortesi, A., Kikic, I., Alessi, P., Turtoi, G. and Garnier, S., "Effect of chemical structure on the solubility of antioxidants in supercritical carbon dioxide: experimental data and correlation," *J. Supercritical Fluids*, **14**, 139 (1999).

Danesh, A., Xu, D.-H., Tehrani, D. H. and Todd, A. C., "Improving predictions of equation of state by modifying its parameters for supercritical components of hydrocarbon reservoir fluids," *Fluid Phase Equilibria*, **112**, 45 (1995).

Gasem, K. A. M., Gao, W., Pan, Z. and Robinson, Jr., R. L., "A modified temperature dependence for the Peng-Robinson equation of state," *Fluid Phase Equilibria*, **181**, 113 (2001).

Hong, I. K., Rho, S. W. and Lee, K. S., "Modeling of soybean oil bed

extraction with supercritical carbon dioxide," *Korean J. Chem. Eng.*, **7**, 40 (1990).

Kim, Y. S., Choi, W. Y., Jang, J. H., Yoo, K.-P. and Lee, C. S., "Solubility measurement and prediction of carbon dioxide in ionic liquids," *Fluid Phase Equilibria*, **228**, 439 (2005).

Mohsen-Nia, M., Modarress, H. and Mansoori, G. A., "A cubic hard-core equation of state," *Fluid Phase Equilibria*, **206**, 27 (2003).

Mojca Škerget, Zorka Novak-Pintarič, Željko Knez and Zdravko Kravanja, "Estimation of solid solubilities in supercritical carbon diox-ide: Peng-Robinson adjustable binary parameters in the near critical region," *Fluid Phase Equilibria*, **203**, 111 (2002).

Noh, M. J., Kim, T. G, Hong, I. K. and Yoo, K.-P., "Measurements and correlation of effect of cosolvents on the solubilities of complex molecules in supercritical carbon dioxide," *Korean J. Chem. Eng.*, **12**, 48 (1995).

Yener, M. E., Ozkal, S. G. and Bayındırlı, L., "Mass transfer modeling of apricot kernel oil extraction with supercritical carbon dioxide," *J. Supercritical Fluids*, **35**, 119 (2005).