

Prediction of the Solubility of Benzoic Acid in Supercritical CO₂ Using the PC-SAFT EoS

Hamidreza Bagheri, Alireza Shariati

Abstract—There are many difficulties in the purification of raw components and products. However, researchers are seeking better ways for purification. One of the recent methods is extraction using supercritical fluids. In this study, the phase equilibria of benzoic acid-supercritical carbon dioxide system were investigated. Regarding the phase equilibria of this system, the modeling of solid-supercritical fluid behavior was performed using the Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT) and Peng-Robinson equations of state (PR EoS). For this purpose, five PC-SAFT EoS parameters for pure benzoic acid were obtained using its experimental vapor pressure. Benzoic acid has association sites and the behavior of the benzoic acid-supercritical fluid system was well predicted using both equations of state, while the binary interaction parameter values for PR EoS were negative. Genetic algorithm, which is one of the most accurate global optimization algorithms, was also used to optimize the pure benzoic acid parameters and the binary interaction parameters. The AAD% value for the PC-SAFT EoS, were 0.22 for the carbon dioxide-benzoic acid system.

Keywords—Supercritical fluids, Solubility, Solid, PC-SAFT EoS, Genetic algorithm.

I. INTRODUCTION

IN the past decades, the chemical industries are forced to reduce the waste of chemicals, environmental pollution, and energy consumption in different processes [1]-[3]. The ideal condition for an environmental chemical process is one in which no solvent is used but most of the chemical processes are solvent-dependent. The supercritical fluids are green solvents which can be used [4]-[6]. The increasing demands of the various industries to solvents which can be rapidly extracted and reused and also solvents which have environmental and economical advantages, are the main points for the use of supercritical fluids [5], [7]. One of the applications of supercritical fluids is the extraction of solid materials using supercritical fluids in which has attracted a lot of attention in various disciplines such as pharmaceutical industries, food industries, oil industries, and etc. Because of the unusual properties of supercritical fluids near their critical point, the density of them could change from gas- like to liquid-like and vice versa [8]-[12]. The transitional feature and the solvency power of these types of fluids are, respectively, like gases (high penetration and low viscosity) and the liquid solvents. The choice of supercritical solvent is the main issue in designing a supercritical fluid extraction process [10]-[14]. By choosing an appropriate solvent, the operational costs would decrease and the purity of the products would increase.

Alireza Shariati (Corresponding author) and Hamidreza Bagheri are with the School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran (Tel.: +98-711-6133704; e-mail: shariati@shirazu.ac.ir).

The solvent should be cheap, non-toxic, non-flammable, and should have an appropriate critical level and solubility. Having all the conditions, carbon dioxide is preferred to other supercritical fluids. It should be added that other fluids such as ethane and ethylene which have low critical temperature and pressure also have been emphasized [15], [16].

As it was mentioned above, the dissolution process of supercritical fluids is like the liquids and the transitional and penetration properties are like the gases; therefore, the phase extraction and separation would be much faster than the situation in which the typical extraction process takes place [12], [17].

In the studies carried out on extraction by means of supercritical fluids, various equations of states have been used- some of them were semi-empirical. These models do not need supercritical properties for estimating the solubility; however, due to the high pressure condition, the semi-empirical equations could not anticipate the solubility of solids appropriately [18]-[20]. Because of the calculation simplicity of the cubic equation of state, several scholars have used it in the modeling of supercritical solid- fluid. However, at high pressure, these types of equations also have difficulties originating from the weak molecular bases.

Recently, several equations of state have been proposed based on the statistical thermodynamics, since they play a significant role in modeling and simulation of thermodynamic systems. The so-called SAFT EoS, present a state of the molecule which is close to the real one [21], [22]. The applications of these types of equations in studying the supercritical fluid-solid systems have attracted a lot of attention and have presented relatively good results [23], [24].

In this work, the solubility of benzoic acid in carbon dioxide has been studied using the PC-SAFT EoS. The simulation results were also compared with the PR EoS.

II. THERMODYNAMIC MODELING

In this section, the equilibrium of a pure solid (species 1; solute) with the supercritical phase containing the species 1 (the solute) and a supercritical solvent (species 2), which is assumed not to be solved in solid phase, will be studied. Since the species 2 is the main species of the supercritical phase, it is usually called the solvent. Since Species 2 does not distribute between the two phases, therefore, a single equation of phase equilibrium for the system could be written:

$$f_1^{Pure\ solid} = \hat{f}_1^{Supercritical} \quad (1)$$

The fugacity of the solid phase can be calculated by [25]:

$$f_1^{Pure\ solid} = \phi_1^{sat} P_1^{sat} \exp\left[\int_{P_1^{sat}}^P \left(\frac{v_1^s}{RT}\right) dp\right] \quad (2)$$

In which the P_1^{sat} is the saturation or sublimation pressure at the system temperature v_1^s is the molar volume of the solid, R is the universal gas constant, and ϕ_1^{sat} is the fugacity coefficient of the pure solute at the sublimation temperature which is usually assumed to be one.

If the molar volume of the solid is assumed to be a weak function of pressure, the (2) will be [25]:

$$f_1^{Pure\ solid} = \phi_1^{sat} P_1^{sat} \exp\left(\frac{v_1^s(P-P_1^{sat})}{RT}\right) \quad (3)$$

and the fugacity of the species 1 in supercritical phase would be [25]:

$$\hat{f}_1^{Supercritical} = y_1 P \hat{\phi}_1^{Supercritical} \quad (4)$$

In which P is the system pressure and $\hat{\phi}_1^{Supercritical}$ is the fugacity coefficient of the species 1 in the supercritical phase. The combination of (3) and (4) and calculating them by considering y_1 would result to [25]:

$$y_1 = \frac{P_1^{sat}}{P} E_1 \quad (5)$$

Since E_1 is usually larger than unity, it is called enhancement factor which is equal to [25]:

$$E_1 = \frac{\phi_1^{sat}}{\hat{\phi}_1^{Supercritical}} \exp\left(\frac{v_1^s(P-P_1^{sat})}{RT}\right) \quad (6)$$

Using ϕ_1^{sat} and $\hat{\phi}_1^{Supercritical}$, E_1 would indicate that vapor phase is non-ideal and by means of Poynting factor, it would indicate the effect of pressure on solid fugacity [25]. The P^{sat} in (5) and (6) is calculated by Antoine equation.

$$\ln P^{sat} = A - \frac{B}{T(K)+C} \quad (7)$$

$\hat{\phi}_1^{Supercritical}$ should be calculated using an equation of state.

III. EQUATION OF STATE

The equation of state plays a significant role in engineering designing. Demanding the least amount of data, cubic equations of state are the simplest type of equations in modeling the solubility [26]. In this paper, the PR EoS has been chosen among the cubic equations of state. This equation only needs the critical properties and a centric factor of the components [27]. The physical properties of benzoic acid and carbon dioxide have been presented in Table I.

TABLE I
 THE PHYSICAL PROPERTIES OF THE COMPOUNDS USED IN THIS WORK

Compound	T_c	P_c	ω	v_c	Ref
Benzoic acid	751	44.7	0.603	96.5	[18]
CO ₂	304.2	73.83	0.224	-	[25]

Since 1980s, when the SAFT EoS was presented by Chapman et al, the different terms used in this equation have undergone several changes and some other terms were also added to it with respect to the type of systems to be studied [28].

In 2001, Gross and Sadowski proposed the perturbed hard-chain model of the SAFT EoS which is known as PC-SAFT EoS. In this model, the reference fluid, the selected hard sphere, and the perturbed theory of the Barker and Henderson selected from the second term, was added. The PC-SAFT EoS is based on the fact that the Helmholtz energy could be introduced as a set of individual statements in which not only the effects of short range repulsive forces and long range gravity forces have been considered but also two chemical bond and intermolecular associations were added. The general form of the equation will be [29]:

$$\frac{A^{res}}{NkT} = \frac{A^{hs}}{NkT} + \frac{A^{disp}}{NkT} + \frac{A^{chain}}{NkT} + \frac{A^{assoc}}{NkT} \quad (8)$$

IV. RESULTS

The CO₂- benzoic acid system was studied in this work. The results of our calculations have been presented in Figs. 1 and 2. Having hydrogen bonding, the benzoic acid has association sites. At low pressures, the solubility of solids in supercritical fluids is low and as the pressure increases, the solubility also increases due to the increase in the enhancement factor and density of supercritical CO₂. The two equations of state appropriately determined the solubility of benzoic acid in the supercritical CO₂. Also, in Fig. 1, despite the large scattering of experimental data, PC-SAFT EoS predicted the system behavior very well.

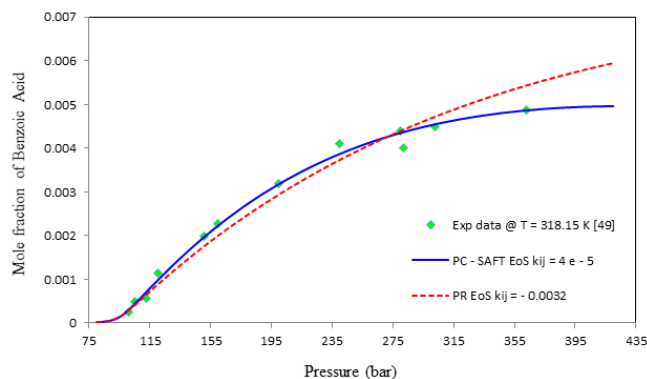


Fig. 1 Solubility of benzoic acid in supercritical CO₂, T = 318.15 K

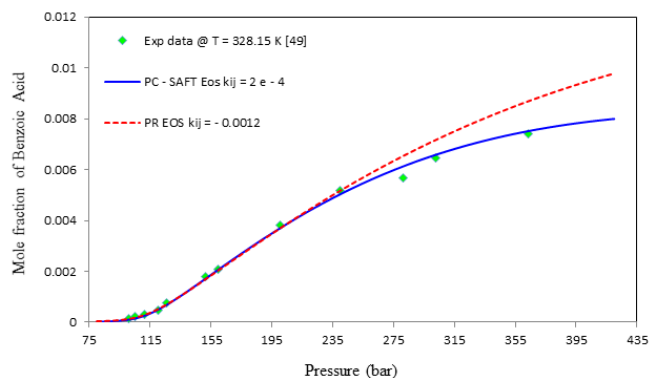


Fig. 2 Solubility of benzoic acid in supercritical CO₂, T = 328.15 K

V. CONCLUSION

In this paper, the solubility of benzoic acid in supercritical carbon dioxide was studied. The solubility results were presented versus pressure at constant temperatures in terms of the mole fraction of the solid in the supercritical phase.

Using the PR and the PC-SAFT as the two equations of state, modeling and simulation of systems were carried out. The constants of the PC-SAFT EoS for benzoic acid with the association bonds, was calculated and other parameters of benzoic acid were used from the previous articles. The results of simulations indicated that the PC-SAFT EoS, which has a stronger basis and theory than the PR EoS, has a better matching with the experimental data. The two equations of state need the k_{ij} parameter to calculate the behavior of systems with components having the association bond.

REFERENCES

- [1] Y. Tanaka and O. Takeshi, "Extraction of Phospholipids from Salmon Roe with Supercritical Carbon Dioxide and an Entrainer", *J. Oleo Sci., Japan Oil Chemists Society*, 53(9): 417-424 (2004).
- [2] M. Ollanketo, K. Hartonen, M. Riekkola, Y. Holm, R. Hiltunen, "Supercritical carbon dioxide extraction of lycopene in tomato skins" (2001), *Eur. Food Res. Technol.* 212 561-565.
- [3] N.L. Rozzi, R.K. Singh, R.A. Vierling, B.A. Watkins, "Supercritical fluid extraction of lycopene from tomato processing byproducts" *J. Agric. Food Chem.* 50 (2002) 2638-2643.
- [4] CL. Phelps, NG. Smart, CM. Wai, Past, "Present and possible future applications of supercritical fluid extraction technology", *J. Chem. Educ.*, 1163: 73 (1996).
- [5] U. Nguyen, D. A. Evans, D. J. Berger, and Calderon, "Process for the Supercritical Extraction and Fractionation of Spices", *US Patent* 5,120,558 (1992).
- [6] M. Gehrig, "Extraction of Natural Material with Carbon Dioxide": Current Applications in Handouts, NATO ASI on Supercritical Fluids IIB Fundamentals and Applications, Kemer, Turkey (1998).
- [7] LiF. and Hsieh, Y. "Supercritical fluid chromatography-mass spectrometry for chemical analysis", *J. Sep. Sci.*, 31, 1231-1237 (2008).
- [8] M. Saito, "History of supercritical fluid chromatography: Instrumental development". *J. Bioengineering*, 590-599, (2013).
- [9] G. Xu, A. M. Scurto, M. Castier, J. F. Brennecke and M. A. Stadtherr, "Reliable computation of high-pressure solid- fluid equilibrium", *Ind. Eng. Chem. Res.* 1624-1636, (2000).
- [10] G. B. Solórzano, "Supercritical fluid technology: computational and experimental equilibrium studies and design of supercritical extraction processes", *Ph.D. Thesis, Graduate School, University of Notre Dame, USA*, (2004).
- [11] M. N. Ponte, "The thermodynamics of supercritical fluids, Science and Technology Faculty", *Nova de Lisbon University, Portugal*.40-42, (2001).

- [12] B. Francesca, D. V. Sara, and G. Fausto, "Supercritical extraction column for separation of limonene and citral", *Paper no. 782, University of Roma, Italy*, (2000).
- [13] Q. Li, Z. Zhang, C. Zhong, Y. Liu, Q. Zhou, "Solubility of solid solutes in supercritical carbon dioxide with and without co-solvents", *Fluid Phase Equilibrium*. 207 (2003) 183-192.
- [14] M.J. Periago, F. Rincon, M.D. Aguera, G. Ros, "Mixture approach for optimizing lycopene extraction from tomato and tomato products", *J. Agric. Food Chem.* 52 (2004) 5796-5802.
- [15] R. Prasad, and H. J. Grubbs, "Process and Apparatus for the Semi continuous Extraction of Nicotine from Tobacco", *US Patent* 5,497,792(1996).
- [16] C.S. Yeh, T. Yu, and A. Berthod, "Separation of steroids by countercurrent chromatography using supercritical fluid carbon dioxide", *J. Liq. Chrom. And Rel. Technol.* 22, 345-356(1999).
- [17] X. Xu, T. D. Veenstra, S. D. Fox, J. M. Roman, H. J., Issaq, R. Falk, J. E. Saavedra, L. K. Keefer, and R. G. Ziegler, "Measuring fifteen endogenous estrogens simultaneously in human urine by high-performance liquid chromatography- mass spectrometry", *Anal. Chem.*, 77, 6646-6654 (2005).
- [18] Z. Yu, B. Singh, S.S.H. Rizvi, J.A. Zollewg, "Solubilities of fatty acids, fatty acid esters, and fats and oils in supercritical carbon dioxide", *J. Supercrit. Fluids* 7 (1994) 51.
- [19] R. Murga, M. T. Sanaz, S. Beltran, and J. L. Cabezas, "Solubility of three Hydroxycinnamic Acids in Supercritical Carbon Dioxide", *J. Supercrit. Fluids* 27 (2003) 239-245.
- [20] S. X. Yang, H. Li, and J. Shi, "Modeling of supercritical fluid extraction by neural networks", *Intelligent Automation and Soft Computing*, 3-12, (2003).
- [21] T. Wang, M. Barber, I. Hardt, and D. B. Kassel, "Mass-directed fractionation and isolation of pharmaceutical compounds by packed-column supercritical fluid chromatography/mass spectrometry", *Rapid Commun. Mass Spectrom.* 15, 2067-2075 (2001).
- [22] C. H. Harris, "Product review: the SFC comeback", *Anal. Chem.*, 74, 87A-91A (2002).
- [23] H. Yang, C. Zhong, "Modeling of the solubility of organic compounds in supercritical carbon dioxide - cosolvent system using SAFT equation of state", *J. Supercrit. Fluids* 33 (2005) 99-106.
- [24] D. M. Kassim, D. Al-Sammerrai, and F. Paulus, "Near critical carbon dioxide extraction of oxidation products from base stock mineral oils", *Sep. Sci. Tech.* 157-164, (1987).
- [25] J.M. Smith, H.C. Van Ness, M.M. Abbott, "Introduction to Chemical Engineering Thermodynamics", *McGraw-Hill, 7th edition, New York*, (2005).
- [26] P. Coimbra, M. H. Gil, C. M. M. Duarte, B. M. Heron, and H. C. de Sousa, "Solubility of a Spiroindolinonaphthoxazine photo chromic dye in Supercritical carbon dioxide: Experimental determination and correlation", *Fluid Phase Equilibrium*, 120-128 (2005).
- [27] A. Danesh, "PVT and phase behaviour of petroleum reservoir fluids" *Elsevier Science, 1th, Amsterdam*, (1998).
- [28] Huang, S. H., Radosz, M., "Equation of state for small, large, polydisperse, and associating molecules" *Ind. Eng. Chem. Res.* (1990), 29, 2284-2294.
- [29] J. Gross, G. Sadowski, "Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules", *Ind. Eng. Chem. Res.*, 2001, 40, 1244-1260.