

APPLICATIONS OF SSAFT EOS FOR DETERMINATION OF THE SOLUBILITIES OF SOLID COMPOUNDS IN SUPERCRITICAL CO₂

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ABSTRACT

Using statistical thermodynamics such as Simplified SAFT equation of state (SSAFTEoS) for estimating phase equilibrium and fluid properties of different materials have been used widely. SSAFT EoS has been developed for associative and non-associative compounds. At high pressure inter molecular forces are very important, on the other hand, in spite of the fact that SSAFT EoS has strength theoretical foundation, it can predict the behavior of high pressure systems. In this research, four solid solubility of benzoic acid, naphthalene, pyrene and Phenanthrene in supercritical carbon dioxide have been studied, SSAFT EoS has been used for modeling. At the end the results have been compared with experimental data. The highest and the absolute average deviation error (AAPD), for carbon dioxide - Phenanthrene and benzoic acid - carbon dioxide systems have been reported 2.22 and 4.43 respectively.

Keywords: SSAFT EoS; Supercritical carbon dioxide; Solid compounds; Solubility.

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1. INTRODUCTION

Today, a growing desire to develop alternative technologies to reduce the adverse effects on the environment has emerged. These include measures to reduce energy consumption, reduce the level of toxic waste, the better use of by-products, and improved quality and safety of end products. High-pressure technologies create processes that produce new products with specific characteristics. Supercritical fluids are substances which temperature and pressure are above the critical temperature and pressure. This was discovered in 1822 by Cagniard and colleagues during a liquid heating test [1]. The transport properties of supercritical fluids are the same as gases (i.e. high permeability and low viscosity) and their solubility resemble those of liquid solvents. Due to these properties, supercritical fluids are used in a wide range of purification, extraction and separation processes [2]. Processes involving supercritical fluids are sustainable, eco-friendly, cost-effective and provide numerous possibilities to produce new products. The major advantage of supercritical fluids is the possibility of the drying of products and their separation with a simple expansion; moreover the recovered gas can be reused without the need for purification. Environmental benefits of using supercritical fluids in industrial processes are less energy consumption during the process and they can potentially be used as alternatives for environmentally destructive organic solvents. Therefore supercritical fluids are called green solvents [3]. Their most important advantages can be seen in the use of supercritical fluids such as carbon dioxide and water. These fluids are non-carcinogenic, non-toxic, non-inflammable and also thermodynamically stable. Another advantage of supercritical fluids is that the physical properties such as permeability, viscosity, density or dielectric constant can be set easily by changing pressure or operating temperature [4]. By choosing a suitable solvent, operating costs reduced and purity of the products increased. Solvent should be Inexpensive and non-toxic and should have a high solubility. Based on the experiences gained in design of a supercritical process, carbon dioxide is usually the first choice. Carbon dioxide is inexpensive, widely available, non-toxic, non-flammable; inert chemically suitable for use in food and pharmaceutical processes and has good critical situations (31.3 °C and 72.9 atm) is [5]. Given the characteristics of supercritical fluids and increasing use of them, modeling and simulating these types of systems is of particular

importance. Also, due to high pressure and importance of intermolecular forces at high pressures, finding equation that can predict the behavior of these systems as well, has great importance [6]. Among the work done in the field of extraction using supercritical fluids, different modes of equations is used in a number of semi-empirical equations. Due to the high pressure, semi-empirical equations can not predict the solubility of solids as well.

The cubic equations of state have been used by many researchers because of their simplicity, but these equations face problems at high pressures. 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 Simplified statistical associating fluid theory (SSAFT EoS), present a state of the molecule which is close to the real one [7]. Benzoic acid and carbon dioxide supercritical systems by assuming ideal behavior for supercritical phase have been modeled by Kurnik and colleagues in the early 90s with low accuracy results. They also modeled this system with PR EoS. The results were reported by binary negative interaction parameter. Coimbra and colleagues used SRK EoS for predicting solubility of solids in supercritical carbon dioxide [8]. Yang and Zhong examined little aromatic solubility in supercritical fluid carbon dioxide by two SSAFT and PR EoS. They mentioned that SSAFT EoS matches with experimental results better than PR EoS [9]. Vaferi and colleagues investigated some aromatic solubility in supercritical fluid carbon dioxide by SSAFT EoS and neural network [10]. Bagheri and Shariati investigated solubility of benzoic acid in supercritical carbon dioxide using the PR and PC-SAFT EoS. The results of PC-SAFT EoS had good adjustment with the experimental data. k_{ij} value for the PR and PC-SAFT EoS was reported negative and positive respectively. In this study, the solubility of different solids in supercritical carbon dioxide has been studied. This was done by SSAFT EoS and the results of modeling have been compared with experimental data. Benzoic acid due to the hydrogen bonds needs to have associative, so each of the five parameters of SSAFT EoS has been used.

2. Thermodynamic modeling

Semi-empirical equation was developed in the late 80th century that was considered a lot by

academic and industrial communities. This equation has been named Statistical association fluid theory by Chapman and colleagues at Cornell University and was presented on the basis of thermodynamic perturbation of Wertheim. Wertheim derived his theory by expanding the Helmholtz energy in a series of integrals of molecular distribution functions and the association potential. On the basis of physical arguments, Wertheim showed that many integrals in this series must be zero and, hence, a simplified expression for the Helmholtz energy can be obtained. The key result of Wertheim's theory is a relationship between the residual Helmholtz energy due to association and the monomer density. In general, SSAFT EoS is not unchangeable equation that only is written in one form but also a way to evaluate the effect of the accumulation of different molecules. The parameters of this equation were obtained to calculate a wide range of fluids including organic matter, light gases, water and polymers. Many efforts in the past decade were done to improve and develop the EoS for increasing its accuracy for different systems [1]. In reviewing the statistical thermodynamics and Grand Canonical sets that all thermodynamic properties can be calculated by use of the Helmholtz energy.

The SSAFT 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 [7]:

$$\frac{A^{\text{res}}}{NKT} = \frac{A}{NKT} - \frac{A^{\text{ideal}}}{NKT} = \frac{A^{\text{hs}}}{NKT} + \frac{A^{\text{disp}}}{NKT} + \frac{A^{\text{chain}}}{NKT} + \frac{A^{\text{assoc}}}{NKT} \quad (1)$$

Where k is Boltzmann's constant and N is the number of molecules. In Eq.(1), first sentence is contributions of Helmholtz free energy due to the short-range repulsion. At this stage molecules are considered as hard spheres that repel each other and there is no gravitational force between them. The second term of Eq.(1) is contributions of Helmholtz free energy due to long-range attractive forces. These forces are mostly achieved by quantum effects and multi-polar energy. The third term of Eq.(1) is share of the Helmholtz free energy through chemical bonding between atoms and formed links dimmer and the trimmer express or higher.

Finally, the fourth term of Eq.(1) is contribution of Helmholtz free energy due to mutual effects of remained electrons of valence layer. In this model it is assumed that a molecule is made of m pieces of the same size and with diameter τ which is called segment. During the four steps listed energy added to it and a real molecule can be achieved. Fig. 1 shows the trend [7].

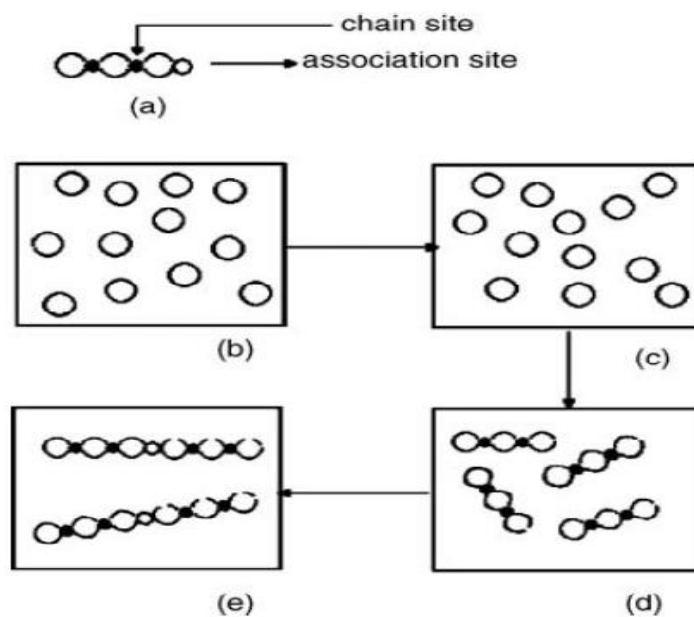


Fig.1. Procedure to form a molecule in the SSAFT model [7].

In general, SSAFT EoS, has five parameters $m, [\epsilon, (u^{\circ}/k), (v/k), K$. These parameters are obtained for pure substances and by a series of equations that are similar to mixing rules, are extended to the mixture. Among these five parameters, two parameters v/k and K was used only for material with association and appears in the equation whenever one of the materials has association property.

In this study, the SSAFT parameters have been used for different materials which are obtained by Huang and Radosz (Table 1). Considering that only benzoic acid has accumulation (hydrogen bonding), the v/k and k parameters for this material is used.

Table1. Pure component parameters of SSAFT EoS [7]

Component	M	θ	u^*/k	ϵ/k	κ
Carbon Dioxide	1.417	13.578	216.08	-	-
Naphthalene	4.671	13.704	304.8	-	-
Pyrene	5.615	18.212	369.380	-	-
Phenanthrene	5.327	16.518	352.0	-	-
Benzoic acid	4.608	12.0	272.660	5930	0.003149

In equilibrium of a pure solid (part 1) with a supercritical fluid and, assuming no solubility of supercritical fluids in solid phase following term can be recited [1].

$$y_1 P \phi_1 = \{ \phi_1^{sat} P_1^{sat} \exp\left(\frac{v_1^{solid} (P - P_1^{sat})}{RT}\right) \} \tag{2}$$

In which P_1^{sat} is the saturation or sublimation pressure at the system temperature and is calculated due to Antoine equation. v_1^{solid} is the molar volume of the solid, R is the universal gas constant, and ϕ_1 is the Fugacity coefficient of component 1 in a supercritical phase that is calculated to help SSAFT EoS (Eq.(3)) [7].

$$\ln \phi_1^v = \frac{\tilde{z}_i^{res}}{KT} - \ln Z \tag{3}$$

$$\frac{\tilde{z}_i^{res}}{KT} = \frac{A^{hc}}{NKT} + \frac{A^{disp}}{NKT} + (Z^{seg} + Z^{chain}) + \frac{\partial}{\partial y_k} \left(\frac{A^{hc}}{NKT} + \frac{A^{disp}}{NKT} \right)_{T,v,y_{j \neq k}} - \sum_{j=1}^N [y_j \left(\frac{\partial}{\partial y_k} \left(\frac{A^{hc}}{NKT} + \frac{A^{disp}}{NKT} \right)_{T,v,y_{j \neq k}} \right)] \tag{4}$$

$$Z = 1 + Z^{seg} + Z^{chain} + Z^{assoc} \tag{5}$$

$$Z^{chain} = (1 - m) \frac{2.5y - y^2}{(1 - y)(1 - 2.5y)} \tag{6}$$

$$Z^{seg} = m \left[\frac{4y - 2y^2}{(1 - y)^3} + \sum_i \sum_j j D_{ij} \left(\frac{u}{KT} \right)^i \left(\frac{y}{z} \right)^j \right] \tag{7}$$

$$Z^{\text{assoc}} = \dots \sum_{A_i} \left[\frac{1}{X^{A_i}} - 0.5 \right] \frac{\partial X^{A_i}}{\partial \dots} \quad (8)$$

The most important parameter in Eq. (8), is " X^A ". Before calculating Z^{assoc} , all the non-zero site-site interactions should be defined. In order to select a proper expression for X^A from Table VII, one has to assign association sites and non-zero sitesite interactions [7].

3. RESULTS AND DISCUSSION

Phase equilibrium calculations has been conducted based on the Eq. (2) and using MATLAB software and solubility of solids in supercritical fluid was investigated. The results of modeling have been compared with existing experimental data. The binary interaction (k_{ij}) parameters were obtained using a genetic algorithm. Results are given in the Figs. 2-5. 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. According to Eq. (2) solubility increases as the pressure increase. Reason of increase of solubility with pressure increasing can be that as the solvent situated in the supercritical region because of the changes that is occurred in it's physical properties, the solvent density increases.

However, due to the saturation of the supercritical region, the solubility will not increase by increasing the pressure continuously. Solubility decreases with decreasing pressure. The cause of this decline can be considered as approaching of carbon dioxide to the transition zone and changing to liquid phase. This accuracy can be seen in Figs. 2-5. According to the results of modeling, SSAFT EoS at high pressures due to strong molecular basis is well able to predict the experimental data. The Table 2. shows the Absolute Average deviation (AAPD) for the four systems.

$$\text{AAPD} = \frac{1}{\text{ND}} \sum_{i=1}^{\text{ND}} \left| \frac{y_i^{\text{Exp}} - y_i^{\text{Calc}}}{y_i^{\text{Exp}}} \right| \times 100 \quad (9)$$

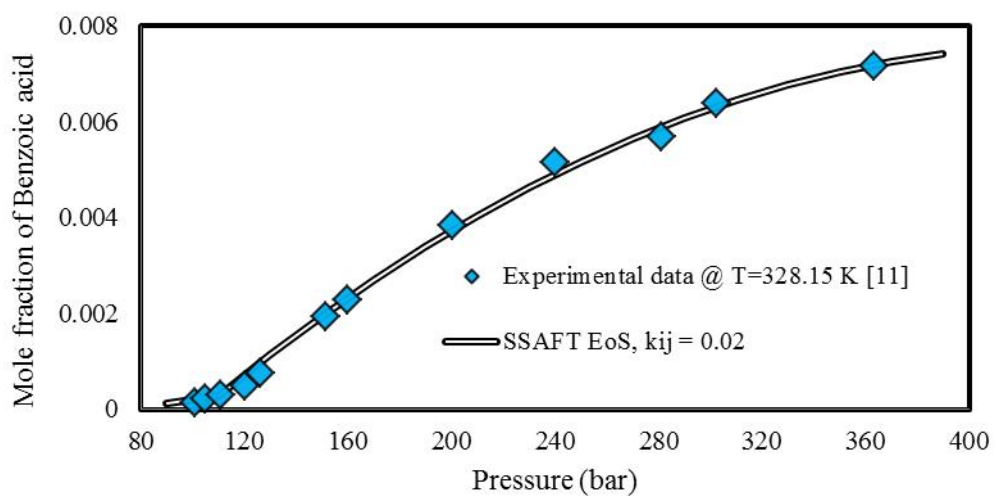


Fig.2. Solubility of benzoic acid in supercritical CO₂

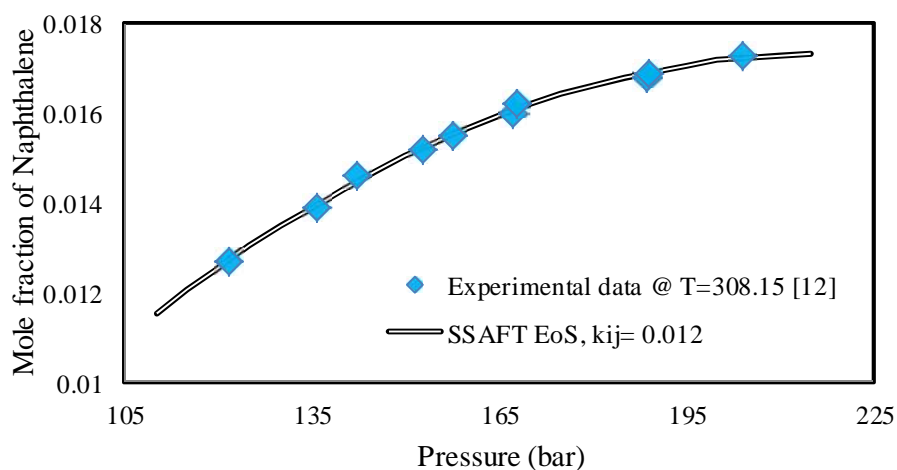


Fig.3. Solubility of naphthalene in supercritical CO₂

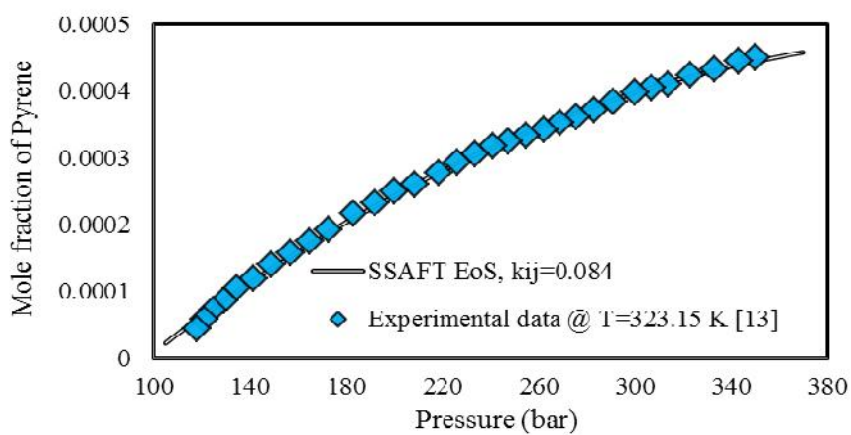


Fig.4. Solubility of pyrene in supercritical CO₂

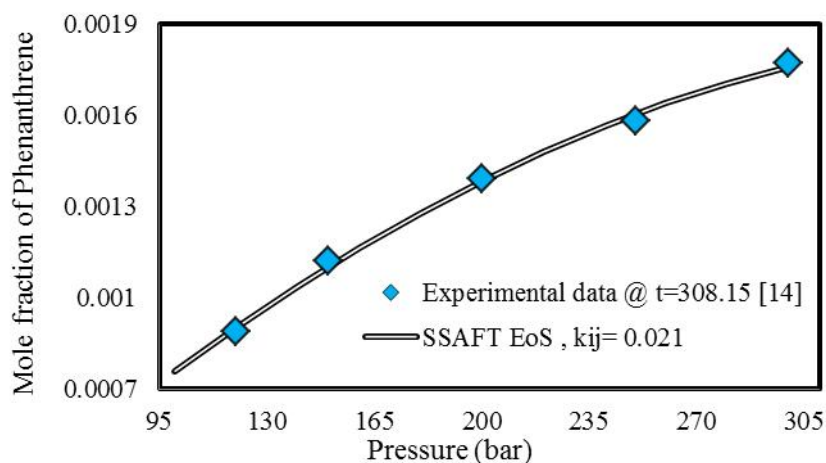


Fig.5. Solubility of phenanthrene in supercritical CO₂

Table 2. Absolute Average deviation estimated amount of supercritical CO₂ -solid systems

System	Number of experimental data	Temperature range (K)	Pressure range (bar)	AAPD	Ref.
Benzoic acid - CO ₂	16	298.15-333.15	80-400	5.26	[11]
Naphthalene - CO ₂	20	300.15-348.15	105-220	4.02	[12]
Pyrene - CO ₂	12	298.15-353.15	100-180	2.48	[13]
Phenanthrene- CO ₂	10	298.15-343.15	95-310	1.75	[14]
-	58	-	-	3.38	-

4. CONCLUSION

In this study, the solubility of solids in supercritical carbon dioxide in the form of four binary system was studied. Due to the high operating pressure, system modeling was done with the help of SSAFT EoS statistics. The simulation results showed that the SSAFT EoS with strong substantial and theory has better compliance with the experimental data. The amounts of 1binary interaction parameter (k_{ij}) were obtained for all systems. According to the researches were done by other researchers, Existing potential in extraction of solid materials with use of supercritical fluids and also for developing behavior of solid-supercritical systems, modeling of extraction systems by use of supercritical fluids can be investigated which needs the help of solvents for increasing the efficiency of the extraction. According to a strong basis of statistical equations theory, other equations of SAFT family can be used.

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