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# Solubilities of Triolein in Supercritical $CO_2$

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The solubilities of triolein in supercritical carbon dioxide were measured over a temperature range of 308−328 K and at pressures between 8 and 20 MPa by the static method. The data were correlated by the model proposed by Chrastil and the modification proposed by Adachi and Lu and Del Valle and Aguilera.

## Introduction

A vegetable oil typically consists of a range of triglycerides, approximately 10% diglycerides, and a small fraction of free fatty acids and other minor constituents (Tilly *et al.*, 1990).

The use of supercritical carbon dioxide for solvent extraction is currently the subject of numerous investigations. Interest in this method of extraction is particularly keen in the food and beverage industry, partly as a result of higher energy costs associated with some other extraction methods but principally because of increasing controls on organic solvents.

Direct experimental determination of solubility data at high pressures requires considerable expenditure in time and equipment. However, in order to establish commercial supercritical fluid extraction (SFE) processes which involve vapor phase extraction, it is important to have reliable equilibrium data and methods for predicting phase equilibrium behavior.

There are two approaches which have been applied to the problem of representing and estimating solubility data at SFE conditions: the use of an expression directly relating the concentration of solute to the solubility parameter or density of the extraction fluid and the use of an equation of state (Adachi and Lu, 1983).

Much effort has been centered on the development of separation and fractionation methods that are clean, efficient, and free of thermal degradation of substances. Despite all the attention given to the application of supercritical carbon dioxide in the fatty oil industry, fundamental data on phase equilibria involving fatty oil and carbon dioxide are still lacking.

In this study, the solubility isotherms of triolein in supercritical (SC) carbon dioxide were measured over a temperature range of 308−328 K and at pressures of 8−20 MPa. Results obtained in the present study are compared with the previously published results.

There are many studies reporting solubilities of fatty acids and esters of fatty acids in SC $CO_2$. Bamberger *et al.* (1988) measured the solubilities of lauric acid, myristic acid, palmitic acid, and triglycerides in SC $CO_2$. Brunetti *et al.* (1989) reported the solubilities of four fatty acids in SC $CO_2$ in the pressure range 20−30 MPa and the temperature range 313−333 K. Chrastil (1982) measured the solubilities of fatty acids and triglycerides in SC $CO_2$ within the pressure range 8−25 MPa and the temperature range 313−353 K, having derived an equation relating the solubility with the density of SC $CO_2$.

The Chrastil model is based on the postulate that the association between solvent and solute molecules results in formation of a solvated complex. The model gives a linear relationship between the logarithm of the solubility and the logarithm of the density of $CO_2$.

$$c = d^k \exp(a/T + b) \qquad (1)$$

$$\ln c = k \ln d + (a/T + b) \qquad (2)$$

where $d$ is the solvent density, $c$ is the solubility, and $T$ is the temperature. The constant $k$, the slope, is an association number which represents the average number of $CO_2$ molecules in the solvated complex and shows the effect of SC $CO_2$ density on the solubility of fatty acids. The constant $a$ depends on the vaporization and solvation enthalpies of the solute. The constant $b$ depends on molecular weights of the solute and $CO_2$, as well as on the value of $k$.

The Chrastil equation has been used to describe the relationship between the solubility and density of carbon dioxide. However, there is some doubt about the physical meaning of the $k$ value determined for the solvated complex.

Adachi and Lu (1983) modified the Chrastil equation by considering the quantity $k$ to be density dependent.

$$k = e_1 + e_2 d + e_3 d^2 \qquad (3)$$

Later Del Valle and Aguilera (1988) presented an improved equation of the Chrastil model for predicting the solubility of vegetable oil in compressed $CO_2$ as a function of temperature and density, which accounts for the variations of the solute's heat of vaporization with temperature.

$$c = \exp(b + m/T + n/T^2)^k \qquad (4)$$

## Equipment and Procedures

High-pressure equilibrium data were obtained using the static apparatus shown in Figure 2. This equipment consists of an equilibrium cell, a feed system, and a sampling system.

The experiment starts with filling the cell (30 $cm^3$, stainless steel) at atmospheric pressure with a small amount (about 2 $cm^3$) of triolein. Liquid $CO_2$ of commercial grade at approximately 50 bar was fed into a hand-operated high-pressure positive displacement pump (HIP-50-6-15). The pump body was cooled to ensure that the $CO_2$ fed into the pump was liquid. This precaution was necessary because the compressibility of the carbon dioxide increases at the critical point, thus reducing the pump efficiency to a degree where effectively no pumping occurs. Before entering the extraction vessel (located inside a water bath),

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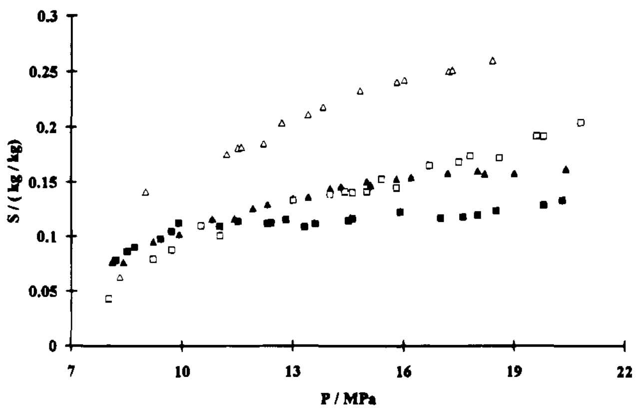

**Figure 1.** Solubility, $S$, of triolein in SC $CO_2$: □, 308 K, 99.95% purity; ■, 308 K, 99.998% purity; △, 313 K, 99.95% purity; ▲, 313 K, 99.998% purity.

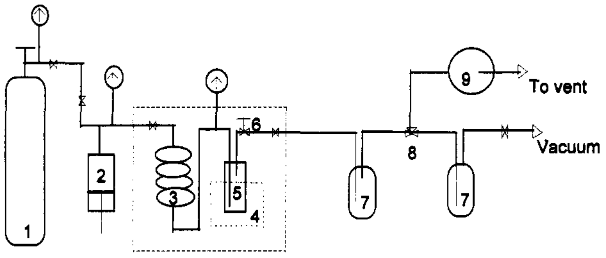

**Figure 2.** Experimental apparatus: (1) $CO_2$ cylinder; (2) high-pressure pump; (3) preheater coil; (4) magnetic system; (5) equilibrium cell; (6) metering valve; (7) trap; (8) three-way valve; (9) dry gas meter.

carbon dioxide from the pump was preheated to the operating temperature by passing it through a stainless steel coil immersed in a constant temperature water bath, controlled to an accuracy of ±0.1 K with a heater circulator (Tectron 3473100, Selecta) and measured with a platinum thermometer with a reported accuracy of ±0.1 K. The pressure of the system was measured by a pressure transducer (Hottinger Baldwin Messtechnick Gmbh, Darmstadt, Germany) with an accuracy of ±20 kPa.

A sufficient mass of carbon dioxide, at the desired pressure and temperature, was then added to the equilibrium cell. Carbon dioxide dissolves in the solutes, so the pressure decreased considerably until the liquid phase was saturated. Thus, more carbon dioxide was added until the desired pressure was reached.

The system was agitated with a magnetic system and a magnetic stirrer for about 2 h, and then the agitation was stopped, allowing the system to equilibrate for about the same time to ensure that the system had reached equilibrium. The equilibated samples were removed from the cell by decompression through a heated metering valve. The liquid solute, which precipitated as a result of the loss in solvent power of carbon dioxide, was collected in a tared trap while the volume of carbon dioxide delivered was measured by a dry test meter (DTM 200A) with an accuracy of ±0.005 L.

The uncertainty of the sample pressure being measured in the pressure readings is less than ±30 kPa, and the temperatures are known within ±0.2 K. Between the sampling valve and the cold trap some solute may condense

**Table 1. Solubility, $S$, of Triolein in $CO_2$**

| pressure/MPa | $S$/(kg of triolein/kg of $CO_2$) | | | | |
|---|---|---|---|---|---|
| | $T = 308$ K | $T = 313$ K | $T = 318$ K | $T = 323$ K | $T = 328$ K |
| 8.0 | | | 0.127 | 0.050 | |
| 8.1 | | 0.077 | | | |
| 8.2 | 0.078 | | | | |
| 8.4 | | 0.077 | | | |
| 8.5 | 0.086 | | 0.140 | | |
| 8.6 | | | | | |
| 8.7 | 0.090 | | | | |
| 9.0 | | | | 0.086 | |
| 9.2 | | 0.096 | | | |
| 9.3 | | | | 0.087 | |
| 9.4 | 0.098 | | | | |
| 9.7 | 0.105 | | | | |
| 9.9 | 0.112 | 0.102 | | | |
| 10.0 | | | 0.162 | 0.089 | 0.080 |
| 10.2 | | | | | 0.087 |
| 10.5 | | | 0.164 | | |
| 10.8 | | 0.116 | | | |
| 11.0 | 0.109 | | | 0.091 | |
| 11.3 | | | | | 0.088 |
| 11.4 | | 0.117 | | | 0.095 |
| 11.5 | 0.114 | | | | |
| 11.8 | | | | | |
| 11.9 | | 0.126 | | | 0.098 |
| 12.0 | | | 0.181 | 0.114 | 0.104 |
| 12.1 | | | 0.180 | | |
| 12.2 | | | 0.171 | 0.107 | |
| 12.3 | 0.112 | 0.130 | | | |
| 12.4 | 0.113 | | | | |
| 12.5 | | | | | 0.108 |
| 12.8 | 0.116 | | | | |
| 12.9 | | | | 0.107 | |
| 13.0 | | 0.135 | 0.188 | 0.118 | 0.117 |
| 13.1 | | | 0.178 | 0.115 | |
| 13.3 | 0.109 | | | | |
| 13.4 | | 0.137 | | | |
| 13.6 | 0.112 | | | | |
| 13.7 | | | | | 0.118 |
| 13.8 | | | 0.177 | | 0.119 |
| 13.9 | | | 0.184 | 0.122 | |
| 14.0 | | 0.145 | | 0.123 | |
| 14.2 | | | 0.193 | | |
| 14.3 | | 0.146 | | | |
| 14.4 | | | 0.199 | | 0.144 |
| 14.5 | 0.115 | | | | |
| 14.6 | 0.117 | | | 0.136 | 0.133 |
| 14.7 | | | | 0.133 | |
| 14.8 | | | | 0.129 | |
| 14.9 | | | 0.202 | | |
| 15.0 | | 0.151 | | 0.136 | 0.137 |
| 15.1 | | 0.147 | | | |
| 15.4 | | | 0.206 | | |
| 15.5 | | | | 0.145 | |
| 15.8 | | 0.153 | 0.212 | | |
| 15.9 | 0.123 | | | | |
| 16.0 | | | | | 0.135 |
| 16.2 | | 0.155 | | | |
| 16.4 | | | | 0.152 | |
| 16.7 | | | 0.225 | | |
| 16.8 | | | | 0.145 | |
| 17.0 | 0.117 | | | | 0.137 |
| 17.2 | | 0.158 | | | |
| 17.6 | 0.118 | | 0.233 | | |
| 17.7 | | | | | 0.146 |
| 18.0 | 0.120 | 0.160 | 0.234 | 0.160 | |
| 18.1 | | | | | |
| 18.2 | | 0.158 | | | 0.131 |
| 18.5 | 0.124 | | | | |
| 18.7 | | | | 0.165 | 0.143 |
| 18.8 | | | 0.239 | 0.166 | |
| 19.0 | | 0.158 | 0.231 | | |
| 19.3 | | | | 0.162 | |
| 19.4 | | | 0.241 | | |
| 19.5 | | | | | 0.145 |
| 19.8 | 0.129 | | | | 0.142 |
| 19.9 | | | | 0.170 | |
| 20.0 | | | 0.234 | | |
| 20.3 | 0.133 | | | | |
| 20.4 | | 0.162 | | | 0.150 |
| 20.9 | | | | 0.166 | |
| 21.0 | | | | 0.175 | |

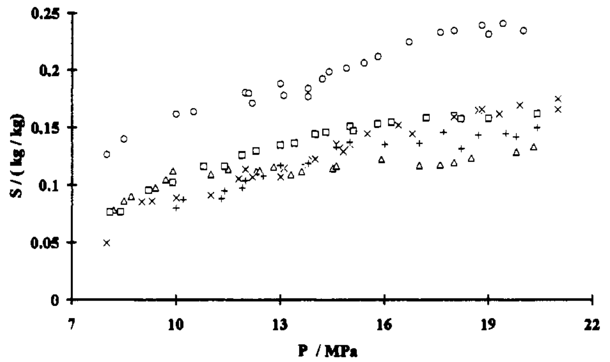

**Figure 3.** Solubility, $S$, of triolein in supercritical $CO_2$ for (△) 308 K, (□) 313 K, (○) 318 K, (×) 323 K, and (+) 328 K.

because flashing may occur during sampling. To remove this solute, the sampling line was washed three times to ensure that all solute was recovered. A vacuum system with a vacuum pump from Edwards High Vacuum Inc. (VEB DSE4) was used as an auxiliary to pull all solvent and solute from the sampling line to the trap. The solvent was then evaporated off in an oven, and the remaining material was measured gravimetrically using an electronic balance with of an accuracy of 0.05 mg. Each solubility was measured five to seven times, and the average value obtained by statistical analysis was used.

The $CO_2$ was supplied by Ar Liquido (Lisboa, Portugal) with stated purities of 99.998% and 99.95%. The triolein was supplied by Sigma Chemical Co. (St. Louis) with a stated purity of 99%. Both materials were used without further purification.

## Results and Discussion

The purity of $CO_2$ is very important in the reproducibility and accuracy of the solubilities. The results obtained in this study with $CO_2$ (99.95% and 99.998% purity) are shown in Figure 1 for data obtained at 308 and 313 K. Solubility data for the binary triolein + carbon dioxide at different temperatures and pressures are presented in Table 1.

Figure 3 shows that the solubility of triolein increases with pressure. The solubility also increases with temperature until near 318 K, decreasing after. The same phenomenon was observed by Tilly *et al.* (1990) in the extraction of triglycerides present in vegetable oils, in the temperature range 313–333 K and pressure range 16–29 MPa. They pointed out that the reason for this is justified by the competition between two effects. As the temperature increases the solute volatility increases, which tends to increase solubility; however, the solvent density decreases, which tends to decrease the solubility. These two effects compete with each other, and one of them will normally be dominant in a particular temperature region. Esquivel (1995) found an increase of the extraction rate of olive husk oil between 310 and 320 K at constant carbon dioxide density (704 kg $m^{-3}$). The extraction rate at constant solvent density was not influenced by the temperature above 320 K, explaining for the increase observed in the presence of lower molecular weight triglycerides.

The triolein solubilities in SC $CO_2$ obtained by Chrastil, the oleic acid solubilities in SC $CO_2$ obtained by Zou *et al.* (1990), and solubilities of fish oil fatty acid ethyl esters in SC $CO_2$ obtained by Staby and Mollerup (1993) together with those obtained in this work are presented in Figures 4 and 5. Some differences can be encountered, although these comparisons show that the Zou *et al.* data and Staby and Mollerup data tend to be similar to those obtained in this work.

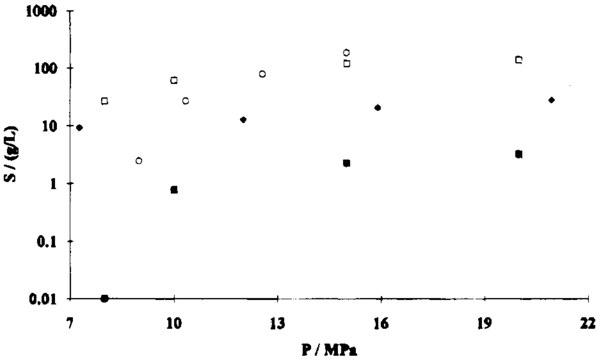

**Figure 4.** Solubility, $S$, of triolein and oleic acid at 313 K: □ this work ◆, Zou *et al.* oleic acid data ■, Chrastil data; ○, Staby and Mollerup, fish oil ethyl ester.

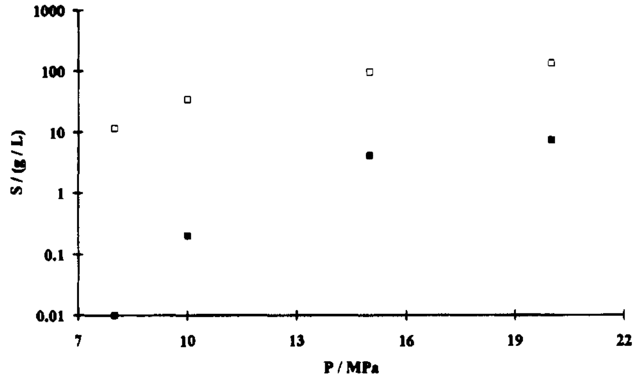

**Figure 5.** Solubility, $S$, of triolein at 323 K: □, this work; ■, Chrastil data.

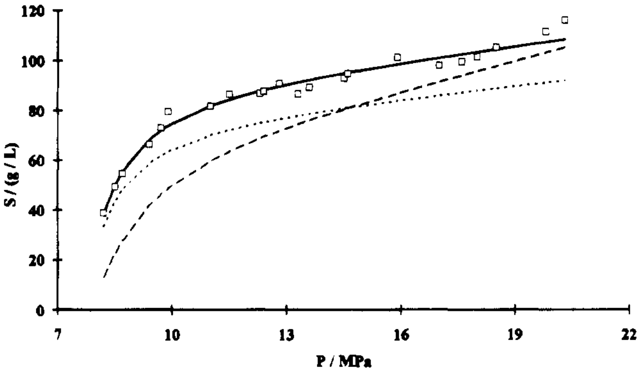

**Figure 6.** Solubility, $S$, of triolein in supercritical $CO_2$ at 308 K: □, experimental data; · · ·, Del Valle and Aguilera equation; - - -, Adachi and Lu equation; —, Chrastil equation.

The solubility data were correlated with the Chrastil and Adachi and Lu equations. The results are compared in Figures 6–10. The model proposed by Del Valle and Aguillera was also used to correlate the results, although the authors recommended the use of their equation in the pressure range of 15–88 MPa. The model of Chrastil provides the best correlation of the experimental data of this work.

Parameters for the three models, optimized by using the Newton method, are presented in Table 2. The $b$ values are similar to those found by Chrastil and other individual authors, which used Chrastil's equation to correlate solubilities, but the constants $k$ and $a$ differ considerably. The significative discrepancy in the association number suggests that Chrastil's model based on solute–solvent interaction in the supercritical fluid phase cannot completely predict the solubility of fatty acids in SC $CO_2$. Nevertheless, this model is simple and has been used successfully to describe the effect of temperature and pressure on the

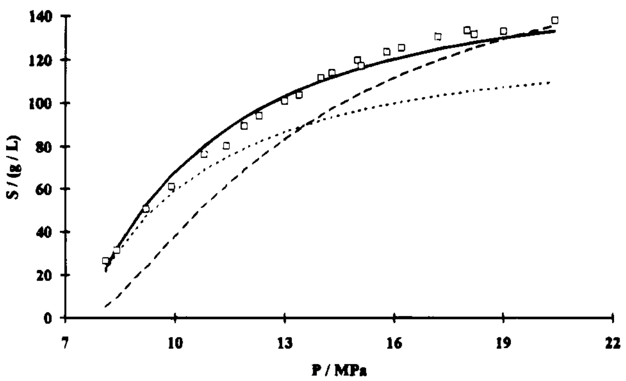

**Figure 7.** Solubility, $S$, of triolein in supercritical $CO_2$ at 313 K; □, experimental data; ···, Del Valle and Aguilera equation, - - -, Adachi and Lu equation; —, Chrastil equation.

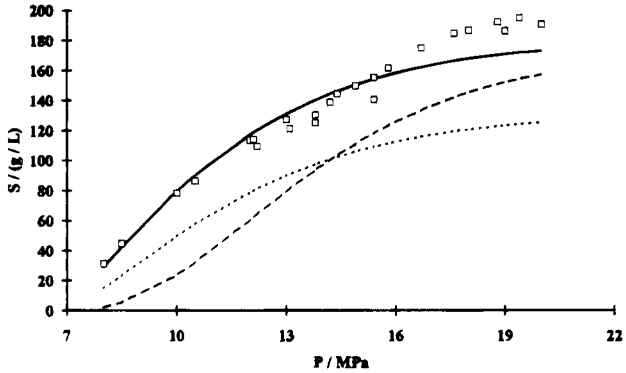

**Figure 8.** Solubility, $S$, of triolein in supercritical $CO_2$ at 318 K: □, experimental data; ···, Del Valle and Aguilera equation; - - -, Adachi and Lu equation; —, Chrastil equation.

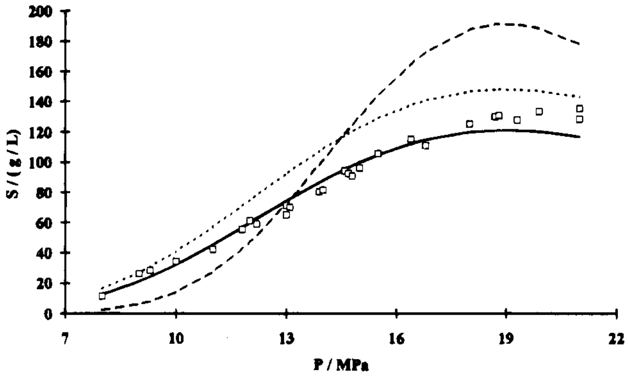

**Figure 9.** Solubility, $S$, of triolein in supercritical $CO_2$ at 323 K: □, experimental data; ···, Del Valle and Aguilera equation - - -, Adachi and Lu equation; —, Chrastil equation.

solubility of various nonpolar compounds (Barath *et al.*, 1992; Foster *et al.*, 1991). Chrastil's model can be used to predict the relationship between the solute solubility and the density of supercritical fluid without assigning a particular physical meaning to the constants $k$, $a$, and $b$.

There are significant discrepancies between the solubility isotherms obtained in this work and those reported previously (Chrastil, 1982; Adachi and Lu, 1983; Del Valle and Aguillera, 1988). The differences between the solubility isotherms obtained by Zou *et al.* (1990) are small compared to the data obtained in this study, but 1 order of magnitude higher than those obtained by Chrastil. The solubilities obtained by Staby and Mollerup (1993) are within the same range as those presented in this work.

It is possible that the observed differences could be the result of either positive or negative enhancement effects caused by impurities present, but also due to undetected phase changes and oversaturation and emulsification phenomena occurring in dense gas solutions during the runs. The sample technique used can also contribute to errors in measuring solubilities, because some liquid or solid can clog the metering valve in the decompression. Besides, in the pressure range 8–12 MPa carbon dioxide is not a good heat transfer medium and its density is very sensitive to pressure and temperature.

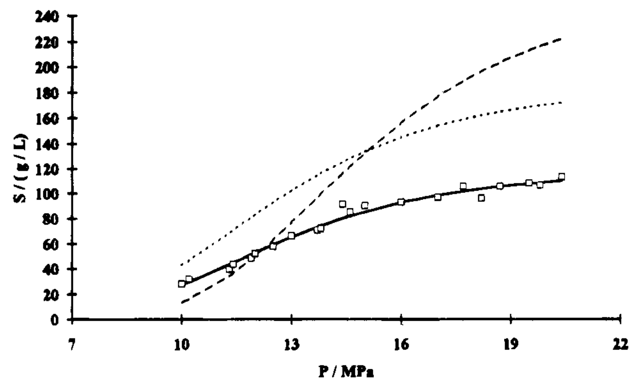

**Figure 10.** Solubility, $S$, of triolein in supercritical $CO_2$ at 328 K: □, experimental data; ···, Del Valle and Aguilera equation; - - -, Adachi and Lu equation; —, Chrastil equation.

**Table 2. Solubility Constants in Carbon Dioxide**

| Chrastil | Adachi | Del Valle |
|---|---|---|
| $k = 1.78$ | $e_1 = 3.32$ | $b = 41.0$ |
| $a = -3.07 \times 10^3$ | $e_2 = 1.04 \times 10^{-4}$ | $m = -1.83 \times 10^4$ |
| $b = 2.53$ | $e_3 = -2.32 \times 10^{-8}$ | $n = 2.20 \times 10^6$ |
| | $a = -6.40 \times 10^3$ | $k = 1.80$ |
| | $b = 2.50$ | |

However, studies with pure compounds providing useful information regarding the effect of pressure and temperature on their solubilities are presented. Simple models such as those of Chrastil (1982), Adachi and Lu (1983), and Del Valle and Aguillera (1988) could serve as the guideline for choosing the appropriate operating conditions or predicting the effect of the pressure and temperature of SC $CO_2$ on the component solubility and extraction yields, after the calculation of their constants.

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## Literature Cited

Adachi, Y.; Lu, B. C.-Y. Supercritical Fluid Extraction with Carbon Dioxide and Ethylene. *Fluid Phase Equilib.* **1983**, *14*, 147–156.

Bamberger, T.; Erichson, J. C.; Cooney, C. L.; Kumar, S. K. Measurement and Model Prediction of Solubilities of Pure Fatty Acids, Pure Triglycerides, and Mixtures of Triglycerides in Supercritical Carbon Dioxide. *J. Chem. Eng Data* **1988**, *33*, 327–333.

Barath, R.; Inomata, H.; Adschiri, T.; Arai, K. Phase Equilibrium Study for the Separation and Fractination of Fatty Oil Components using Supercritical Carbon Dioxide. *Fluid Phase Equilib.* **1992**, *81*, 307–320.

Brunetti, L.; Dagheta, A.; Fedeli, E.; Kikic, I.; Zanderighi, L. Deacidification of Olive Oils by Supercritical Carbon Dioxide. *J. Am. Oil Chem. Soc.* **1989**, *66*, 209–217.

Chen, Hao; Schwartz, S. J.; Spanos, G. A. Fractionation of Butter Oil by Supercritical Carbon Dioxide. *J. Dairy Sci.* **1992**, *75*, 2659–2669.

Chrastil, J. Solubility of Solids and Liquids in Supercritical Gases. *J. Phys. Chem.* **1982**, *86*, 3016–3021.

Del Valle, J. M.; Aguillera, J. M. An Improved Equation for Predicting the Solubility of Vegetable Oils in Supercritical $CO_2$. *Ind. Eng. Chem. Res.* **1988**, *27*, 1551–1553.

Esquivel, M. M. Supercritical Extraction of Olive Husk Oil. Ph.D. Thesis, Instituto Superior Técnico, Lisboa Codex, Portgual, **1995**.

Foster, N. R.; Yun, S. L. J.; Ting, S. S. T. Solubility of Oleic Acid in Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **1991**, *4*, 127–130.

Goncalves, M.; Vasconcelos, A. M.; Gomes de Azevedo, E. J. S.; Chaves das Neves, H. J.; Nunes da Ponte, M. On the Appliction of Supercritical Fluid Extrction to the Deacidification of Olive Oils. *J. Am. Oil Chem. Soc.* **1991**, *68*, 474–480.

Liang, J. H.; Yeh, A.-I. Process Conditions For Separating Fatty Acid Esters by Supercritical $CO_2$. *J. Am. Oil Chem. Soc.* **1991** *68*, 687–692.

Liong, K. K.; Foster, N. R.; Ting, S. S. T. Solubility of Fatty Acid Esters in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1992**, *31*, 400–404.

Maheshwari, P.; Nikolov, Z. L.; White, T. M.; Hartel, R. Solubility of Fatty Acids in Supercritical Carbon Dioxide. *J. Am. Oil Chem. Soc.* **1992**, *66*, 1069–1076.

Nilson, W. B.; Gauglitz, E. J., Jr.; Hudson, J. K. Solubility of Methyl Oleate, Oleic Acid, Oleyl Glycerols, and Oleyl Glycerol Mixtures in Supercritical Carbon Dioxide. *J. Am. Oil Chem. Soc.* **1991**, *68*, 87–91.

Staby, A.; Mollerup, J. Solubility of Fish oil Fatty Acid Ethyl Esters in Sub and Supercritical Carbon Dioxide. *J. Am. Oil Chem. Soc.* **1993**, *70*, 583–588.

Stahl, E.; Quirin, K.-W.; Gerard, D. Solubilities of Soybean Oil, Jojoba Oil and Cuticular Wax in Dense Carbon Dioxide. *Anstrichmittel* **1983**, *12*, 458–463.

Tilly, R. D.; Chaplin, R. P.; Foster, N. R. Supercritical Fluid Extraction of the Triglycerides Present in Vegetable Oils. *Sep. Sci. Technol.* **1990**, *25*, 357–367.

Yeh, A.-I.; Liang, J. H.; Hwang, L. S. Separation of Fatty Acid Esters from Cholesterol in Esterified Natural and Synthetic Mixtures by Supercritical Carbon Dioxide. *J. Am. Oil Chem. Soc.* **1991**, *68*, 224–229.

Ykushima, Y.; Hatakeda, K.; Ito, S.; Saito, N.; Asano, T.; Goto, T. A Supercritical Carbon Dioxide Extraction from Mixtures of Triglycerides and Higher Fatty Acid Methyl Esters Using a Gas-Effusion-Type System. *Ind. Eng. Chem. Res.* **1988**, *27*, 818–823.

Zou, M.; Lim, S. B.; Rizvi, S. S. H.; Zollweg, J. A. Vapor-Liquid Equilibria of Fatty Acid Esters in Supercritical Fluids. *Supercritical Fluid Science and Technology*; Johnston, K. P., Penninger, J. M. L., Eds.; ACS Symposium Series 406; American Chemical Society: Washington, DC, 1989; Chapter 8, pp 98–110.

Zou, M.; Yu, Z. R.; Kashulines, P.; Rizvi, S. S. H.; Zollweg, J. A. Fluid-Liquid Phase Equilibria of Fatty Acids and Fatty Acid Methyl Esters in Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **1990**, *3*, 23–28.

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