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# Supercritical Fluid−Solid Phase Equilibria Calculations by Cubic Equations of State and Empirical Equations: Application to the Palmitic Acid + Carbon Dioxide System

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The solubility of palmitic acid in supercritical carbon dioxide has been determined experimentally in the pressure range (100 to 350) bar and the temperature range (35 to 55) °C. A cubic equation of state and an empirical equation have been used to correlate the solubility of this fatty acid in supercritical carbon dioxide. The first method, which is based on thermodynamic properties, uses two fitting parameters, the solid sublimation pressure and the binary interaction parameter. The sublimation pressure values obtained have been correlated using the Clapeyron equation. The interaction parameter has been correlated as a function of temperature. The empirical method is based on an equation that relates the solubility of the solid with the operation conditions. The empirical and equation of state methods provide good agreement between theory and experimental results for the solubility of palmitic acid in supercritical carbon dioxide.

## Introduction

In the food industry, the extraction of oils from biological materials and the separation of their components by extraction or division constitutes one of the main applications of supercritical fluids. Our understanding of the properties of palm oil is less detailed than that of more commonly used compounds, despite the fact that palm oil is one of the major edible oils consumed worldwide. Palm oil is used as kitchen oil and in the manufacture of margarines. It has been shown that consumption of this material does not increase cholesterol levels, and it is also rich in vitamins A and E. These important minor components are often destroyed or lost during bleaching and refining processes due to the high temperatures required. In addition, complete removal of solvents is usually expensive and difficult to achieve. Separation of the components present in crude palm oil using supercritical fluids is an attractive technique because selective extraction and separation mean that the product can be easily removed and recovered.[1] Palmitic acid is a representative example of the free fatty acids in palm oil.

The application of supercritical fluid technology to each of the processes described above requires the study of the phase equilibrium formed by each of the solutes and the supercritical solvent, i.e., the fluid−solid phase equilibrium. In the work described here, the experimental solubility of palmitic acid in supercritical carbon dioxide was determined using a dynamic apparatus in the pressure range (100 to 350) bar and the temperature range (35 to 55) °C. This equilibrium has been studied by several authors. In 1988, Bamberger et al.[2] measured the solubility of several free fatty acids, among them the palmitic acid and its corresponding triglycerides, at 40 °C and in the pressure range (80 to 250) bar. In 1989, Oghaki et al.[3] also measured the solubility of this fatty acid in the temperature range (25 to 40) °C in a wide range of pressures. Iwai et al.,[4] in 1991, measured the solubility of this fatty acid at 35 °C. Actually, with the objective to study the solubility of palmitic acid in the mixture $CO_2$ + water, Iwai et al.[5] measured the solubility of this acid in pure $CO_2$ at 40 °C and 150 bar; this value has been compared with that obtained by Oghaki et al., since they are similar.

Empirical and thermodynamic models that employ equations of state and mixing rules to calculate solubilities of fatty acids in supercritical fluids have been widely described.[5−7] The study described here involved correlation of the solubility data using the empirical equation proposed by Yu et al.[5] The thermodynamic model is based on the use of the Soave−Redlich−Kwong[8] (SRK) equation of state (EOS) with van der Waals[8] mixing rules. The Klincewicz and Reid[9] group contribution method was used to estimate the properties of the pure component.

## Experimental Section

The solubility of palmitic acid was determined using the flow-type cylindrical equilibrium cell described previously.[10] The temperature was measured with a type-J thermocouple with a temperature control accuracy of ±0.2 °C. A back-pressure regulator was used to maintain a constant pressure with a pressure control accuracy of ±10 bar.

The use of this apparatus requires a flow-rate study to be performed in order to ensure that carbon dioxide is saturated with the solid. This effect is represented in Figure 1. This preliminary study shows that the best flow rate is around 1 mL·min$^{-1}$. In an attempt minimize the risk of losing portions of the solute, the valves and connection tubing were disconnected after each run and carefully washed with a suitable solvent (in this case isooctane). The solution was then collected, the solvent was evaporated, and the solute was dissolved in 5 mL of solvent to determine its concentration.

Quantitative analysis of the solid dissolved in the organic solvent was carried out by gas chromatography: HP 6890, Nukol (SUPELCO) column (15 m length, 0.53 mm i.d. and 0.5 mm nonpolar film) and FID.

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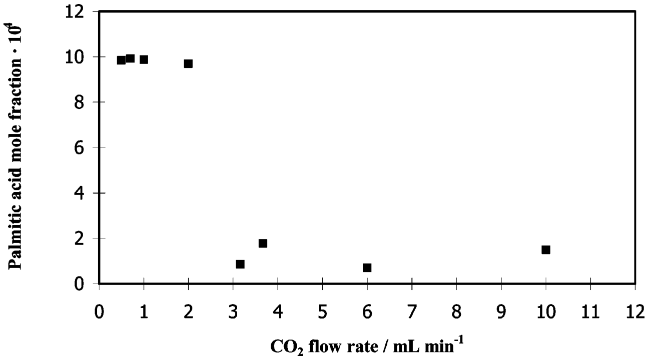

**Figure 1.** Effect of carbon dioxide flow rate on the solubility determination.

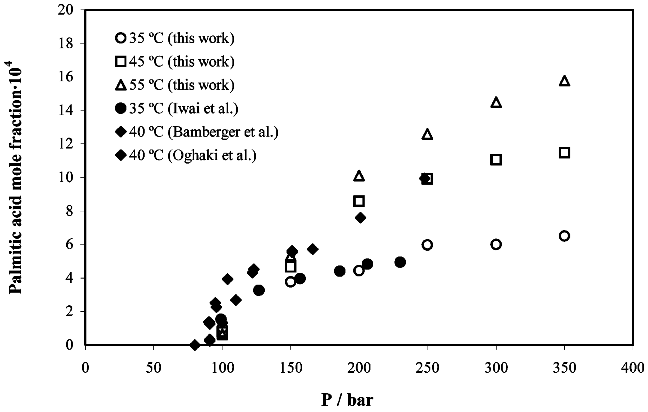

**Figure 2.** Experimental solubility of palmitic acid in supercritical carbon dioxide and solubility data obtained by Bamberger et al.,[2] Oghaki et al.,[3] and Iwai et al.[4]

**Table 1. Solubility of Palmitic Acid in Supercritical Carbon Dioxide (Mole Fraction × $10^4$)**

| $P$/bar | 35 °C | 45 °C | 55 °C |
|---|---|---|---|
| 100 | 1.03 | 0.79 | 0.65 |
| 150 | 3.76 | 4.66 | 5.35 |
| 200 | 4.45 | 8.58 | 10.13 |
| 250 | 5.99 | 9.92 | 12.60 |
| 300 | 6.01 | 11.05 | 14.50 |
| 350 | 6.50 | 11.47 | 15.79 |

## Results and Discussion

***Verification of the Apparatus.*** In a previous study, the reliability of the apparatus was assessed by determining the solubility of naphthalene at (35 to 55) °C at pressures of (120 and 300) bar. This method was used because the solubility data for naphthalene in supercritical carbon dioxide are well known.[10] Agreement was within ±5%.

***Solubility Data.*** The solubility data for palmitic acid in carbon dioxide at (35, 45, and 55) °C at pressures between (100 and 350) bar are shown in Table 1. The observed reproducibility was 5−8%. Our experimental data and data obtained by Bamberger et al., Oghaki et al., and Iwai et al. at their work conditions are shown in Figure 2. It can be seen that the solubility values obtained in this work agree with those obtained by Iwai et al. at 35 °C within ±10%. The results show that the solubility of palmitic acid increases with increasing pressure. At pressures above 150 bar, the solubility increases with increasing temperature. However, at 100 bar, the solubility appears to decrease slightly with the temperature.

***Modeling.*** An empirical model and a thermodynamic model have been selected to correlate the equilibrium data.

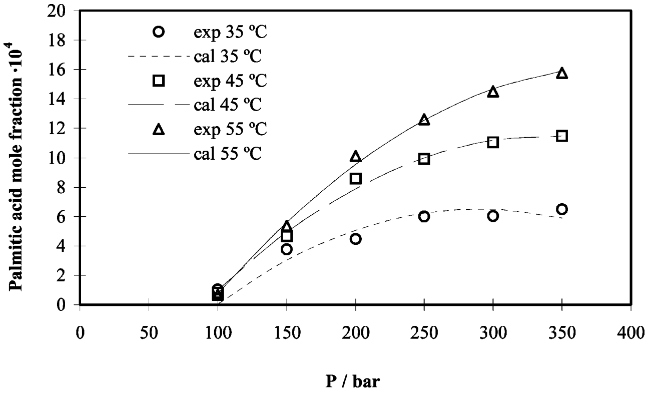

**Figure 3.** Solubility of palmitic acid in supercritical carbon dioxide; experimental data and results obtained using the equation of Yu et al.[5]

**Table 2. Calculated Regression Parameters and Deviation for the Yu et al.[5] Equation**

| | Yu et al. equation |
|---|---|
| $b_0$ | $-5.74 \times 10^{-2}$ |
| $b_1$ | $-4.81 \times 10^{-5}$ |
| $b_{11}$ | $-1.80 \times 10^{-8}$ |
| $b_2$ | $3.70 \times 10^{-4}$ |
| $b_{22}$ | $-6.06 \times 10^{-7}$ |
| $b_{12}$ | $1.90 \times 10^{-7}$ |
| $R^2$ | 0.9913 |
| AARD (%) | 12.32 |

***1. Empirical Model.*** Several models have been described in the literature, and the Yu et al.[5] equation was selected to correlate the solubility data. This equation is completely empirical and relates the solubility, $y$ (in mole fraction), with pressure, $P$/bar, and temperature, $T$/K

$$y = b_0 + b_1 P + b_{11} P_2 + b_2 + T + b_{22}\, T_2 + b_{12} PT(1 - y) \tag{1}$$

The results obtained on using this equation are presented in Table 2. The errors in the fitting were determined by calculating the average absolute relative deviation (AARD) between the measured and calculated data. It can be deduced from the AARD values that the calculated results are in agreement with the experimental data on using the equation derived by Yu et al. This situation is consistent with the fact that it was developed specifically for fatty acids. However, at 35 °C, this equation shows a wrong trend at higher pressures. The experimental and calculated data for this equation are shown in Figure 3.

***2. Thermodynamic Model.*** The solubility of a nonvolatile solid solute ($y_2$) in a supercritical solvent is determined from standard thermodynamic relationships by equating fugacities in the condensed phase and in the supercritical fluid phase for each component.[11] In this way, the solubility of the solid in supercritical carbon dioxide is

$$y^2 = \frac{P_2^{\mathrm{sat}}}{\hat{\phi}_2^{\mathrm{F}} P} \exp \frac{(P - P_2^{\mathrm{sat}}) V_2^{\mathrm{S}}}{RT} \tag{2}$$

where $P_2^{\mathrm{sat}}$ and $V_2^{\mathrm{S}}$ are the saturation pressure (sublimation pressure in this case) and the molar volume of pure solid, respectively, and $\hat{\phi}_2^{\mathrm{F}}$ is the fugacity coefficient of the solid in the supercritical phase (at pressure $P$ and temperature $T$). The calculation of the solubility $y_2$ therefore requires values for $P_2^{\mathrm{sat}}$, $V_2^{\mathrm{S}}$, and an equation of state (with its associated mixing rules) for the calculation of $\hat{\phi}_2^{\mathrm{F}}$. The SRK equation of state with van der Waals mixing rules

**Table 3. Known and Estimated Physical Properties of Palmitic Acid**

| estimated properties | | ref |
|---|---|---|
| $T_c$/K | 886.61 | 9 |
| $P_c$/bar | 19.86 | 9 |
| $w$ | 0.315 | 8 |
| **known properties** | | **ref** |
| $T_b$/K | 622.30 | 12 |
| $V_m$/cm$^3$ mol$^{-1}$ | 287.2 | 2 |

**Table 4. Fitting Parameters of Experimental Data Using SRK Equation of State and $P_2^{sat}$ Values from Literature Data**

| | SRK | | lit | |
|---|---|---|---|---|
| $t$/°C | $K_{12}$ | $P_2^{sat}$/bar | $P_2^{sat}$/bar$^{16}$ | $P_2^{sat}$/bar$^7$ |
| 35 | −0.098 | $2.51 \times 10^{-10}$ | $1.43 \times 10^{-9}$ | $8.11 \times 10^{-10}$ |
| 45 | −0.059 | $5.00 \times 10^{-9}$ | $9.55 \times 10^{-9}$ | $1.04 \times 10^{-8}$ |
| 55 | −0.041 | $3.10 \times 10^{-8}$ | $5.66 \times 10^{-8}$ | $1.14 \times 10^{-7}$ |
| AARD ($350 \geq P \geq 100$) | 12.89% | | | |
| AARD ($P \geq 200$) | 3.46% | | | |

were used for all calculations.[8] Prior to performing phase equilibrium calculations with such an equation of state, it is necessary to estimate the critical temperature and pressure, as well as the acentric factor, for each pure component. In the case of $CO_2$, the physical properties are known from experimental measurements ($T_c = 304.2$ K, $P_c = 73.8$ bar, $\omega = 0.225$).[11] The critical temperature and pressure of this solid were estimated in this study using a simplified version of the Klincewicz and Reid group contribution method.[9] The acentric factor was estimated using the Lee−Kesler correlation.[8] The known properties (boiling temperature[12] and molar volume[2]) and estimated properties are summarized in Table 3.

For this system, two parameters, the binary interaction parameter ($K_{12}$) (which is part of the van der Waals mixing rules) and the sublimation pressure of palmitic acid ($P_2^{sat}$), were fitted by minimizing the error (AARD) between experimental and calculated solubility data. The use of the sublimation pressure as a fitting parameter has been described by various authors. In 1995, Reverchon suggested such an adjustment model.[13] Cortesi et al. used $P_2^{sat}$ and $K_{12}$ as fitting parameters and also compared the results with those obtained using only $K_{12}$. The resulting values of $P_2^{sat}$ were very found to be similar to those found in the literature.[14] Recently, Huang et al. used this procedure to calculate the solubility of solids, also checking the reliability of the same one with data for systems where $P_2^{sat}$ is known.[7]

In previous works, the solubility of an antibiotic[15] and a disperse dye[10] were determined and the thermodynamic model used was based for fitting the two parameters discussed above. In the case of palmitic acid, the value of the sublimation pressure is known: ($1.43\ 10^{-9}$, $9.55\ 10^{-9}$, and $5.66\ 10^{-8}$) bar at (35, 45, and 55) °C, respectively.[16] It is therefore possible to compare the data obtained using this correlation method with the tabulated data for sublimation pressure. The values of all the parameters used for fitting experimental data are shown in Table 4 along with the literature data for the sublimation pressure. The $P_2^{sat}$ values obtained have been correlated using the Clapeyron equation for the $R^2$ value above 0.9. $K_{12}$ values increase with temperature, and they can be adjusted according to a linear relationship with temperature for an $R^2$ value above 0.9. The experimental data and the data calculated using the equation of state are represented in Figure 4. The data calculated with the EOS are in good agreement with experimental data, as can be observed from Figure 4.

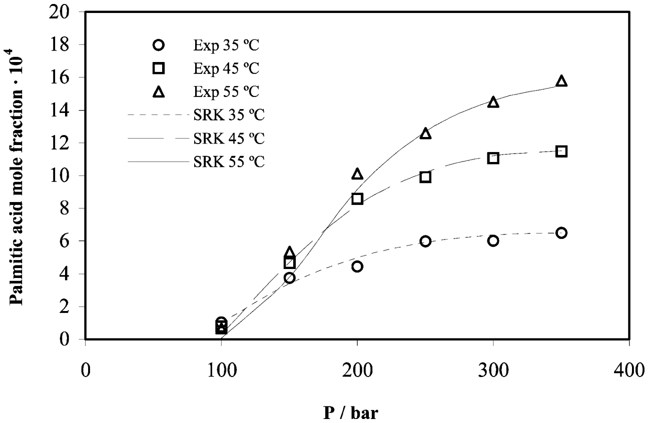

**Figure 4.** Solubility of palmitic acid in supercritical carbon dioxide; experimental results and results obtained using the thermodynamic model with the SRK equation of state.

## Conclusions

The solubility of a fatty acid, namely, palmitic acid, in supercritical carbon dioxide has been determined in the temperature range (35 to 55) °C and the pressure range (100 to 350) bar using a flow-type equilibrium cell. The experimental data agree with those obtained by Iwai et al. at 35 °C. The solubility of the solid in supercritical carbon dioxide can be correlated with an empirical model and a thermodynamic model. The thermodynamic model is based on the SRK equation of state that requires the critical properties and sublimation pressure data for the solid. The critical properties have been estimated using a group contribution method, and the sublimation pressure and binary interaction parameters have been used as fitting parameters. The binary interaction parameter in the correlation was found to be dependent on temperature, and the sublimation pressure obtained was found to adjust to the Clapeyron equation. The calculated results with the empirical equation developed by Yu et al. are in agreement with the experimental data except at 35 °C at higher pressures. And good results in calculated data and in $P_2^{sat}$ values were obtained in the thermodynamic model using the SRK equation of state.

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