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# Phase Equilibria for the Ternary System Methyl Oleate + Tocopherol + Supercritical $CO_2$

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To study the feasibility of using supercritical $CO_2$ to concentrate natural tocopherols from soybean oil deodorizer distillate (DOD), we measured the ternary phase equilibrium data for methyl oleate + α-tocopherol + supercritical $CO_2$ from (313.15 to 353.15) K in the pressure range from (10 to 29) MPa. The measured data were well correlated using the Soave−Redlich−Kwong EOS with the Adachi−Sugie mixing rule. The separation factor between methyl oleate and tocopherol in $CO_2$ was investigated. On the basis of these results, equilibrium lines in the experimental ranges were obtained that provide fundamental data for concentrating tocopherols with supercritical $CO_2$. In addition, because the distribution of tocopherol in supercritical $CO_2$ increases markedly because of the abundance of methyl oleate, methyl oleate was shown to act as a cosolvent for tocopherol. Finally, according to the obtained results, a strategy for a separation operation was suggested. Visual observation also provided information useful in further experiments and design.

## Introduction

Deodorizer distillate (DOD) is a kind of byproduct from the soybean oil refining process. It is rich in natural tocopherols (vitamin E) and sterols, which are widely used in the food and medical industries. Although the conventional methods of vacuum and molecular distillation have been applied in the commercial production of tocopherols from DOD, there are some drawbacks to these approaches: high production cost, unstable quality of products, and so forth.[1] Thus, a new alternative technique is desired.

Supercritical $CO_2$, as a separating solvent, is relatively well suited for extracting some fat-soluble components. Moreover, the low temperature (<373.15 K) employed in the supercritical $CO_2$ process does not damage tocopherols; additionally, the separation selectivity can be easily tuned by changing the pressure, temperature, and reflux ratio. In the successful design of a supercritical $CO_2$ process, research on phase equilibrium is indispensable and fundamental. Because of a shortage of this kind of phase equilibrium data, published operation parameters for concentrating tocopherols in DOD with supercritical $CO_2$ differ from author to author.

To simplify the composition of raw material, methyl esterification and alcoholysis are generally carried out, followed by the removal of most sterols from the esterified system. After treatment, the esterified DOD (ME-DOD) mainly contains fatty acid methyl esters (FAMEs, (70 to 80) mass %), (tocopherols (10 to 15) mass %), and other impurities such as residual sterols, glycerides, squalene, pigments, and long-chain paraffins, all of which comprise about (10 to 15) mass % of the system. When concentrating natural tocopherols from this system, the important step is to remove FAMEs, which contribute more than 70 mass % of ME-DOD. To explore the reasonable operation conditions for this step, the complex system of ME-DOD + $CO_2$ was initially regarded as a pseudoternary (methyl oleate + tocopherol + $CO_2$) system. Because no phase equilibrium data for this ternary system was available in the literature, we carried out measurements with the aim of providing fundamental information for further separation experiments and process design. Methyl oleate was chosen because in the system of ME-DOD obtained from soybean oil, methyl oleate and methyl linoleate (similar to methyl oleate in physicochemical properties) are the main components of FAMEs (about 75 to 80 mass %).[2]

## Experimental Section

***Materials.*** $CO_2$ was supplied from Uchimura Sanso Co. Ltd. (Osaka, Japan) with a purity of 99.97%. Methyl oleate and DL-α-tocopherol were obtained from Wako Pure Chemical Industries Inc. (Tokyo, Japan) with purities of ≥98%; ME-DOD (10.19% tocopherols with 12.05:1.28:60.29:26.38 α, *β*, *γ*, and *δ* isomers) was supplied by Kaidi Fine Chemical Industries Co. Ltd. (Wuhan, Hubei Province, PR China). Because both tocopherols (in ME-DOD) and DL-α-tocopherol (in the mixed feed) were used in this work, for convenience tocopherol represents the target tocopherols in this paper.

***Apparatus and Procedure.*** An experimental apparatus was established for measuring the compositions of both the liquid and gas phases. As shown in Figure 1, the apparatus consists of feed, equilibrium, and sampling systems. A view cell (30 mL, max pressure 30 MPa, Akico Co., Tokyo, Japan) coupled with a magnetic stirrer was employed as the equilibrium vessel, and its temperature was controlled with an electric heater capable of maintaining the temperature to within ±0.1 K.

Initially, the equilibrium cell is charged with about 15 to 20 mL of feed. $CO_2$ then flows into the apparatus from the $CO_2$ tank via the filtering pipe and syringe pump (ISCO 260 D, max pressure 57.71 MPa, ISCO Co., Lincoln, NE), which is operated in constant pressure mode with an uncertainty in pressure of ±0.01 MPa, and into the equilibrium cell. After the pressure and temperature reach the required values, the magnetic stirrer is turned on, and

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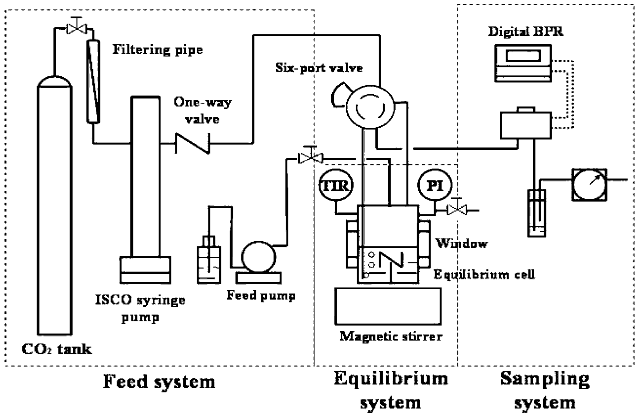

**Figure 1.** Schematic diagram of the phase equilibrium apparatus.

the system inside the equilibrium cell is stirred for at least 2 h. By rotating the six-port valve, the samples are converted to and from gas (light phase) and liquid (heavy phase). For example, the situation shown in Figure 1 applies to taking a sample from the gas phase. During sampling, by adjusting the microswitch of the digital BPR (back-pressure regulator, JASCO 880-81, JASCO International Co. Ltd., Tokyo, Japan), gaseous $CO_2$ passes slowly through the sampling bottle and flowmeter, which records the amount of $CO_2$ (defined as compound 3) consumed. The pipes connected to the six-port valve, cell, and digital BPR are heated by electric heaters. Their temperatures are controlled in a manner similar to that of the equilibrium cell. Additionally, because of the effect of adiabatic expansion, the fluid temperature decreases greatly and suddenly during sampling. Consequently, some solutes or $CO_2$ may condense at the outlet of the BPR, contributing more or less to the measurement inaccuracy. To avoid such phenomena, we heated the BPR outlet and maintained it at a temperature of 371 K. In addition, about 10 mL of *n*-hexane was initially loaded in the sample bottle because the solutes may form aerosol particles and pass through the collecting bottle with the $CO_2$ fluid.[3] The *n*-hexane solution is quantified by an electronic balance (precision $10^{-4}$ g) and analyzed by GC (for methyl oleate, compound 1) and HPLC (for tocopherol, compound 2). According to the amount of $CO_2$ consumed and chromatographic data, the gas composition ($y_1$, $y_2$, $y_3$) is calculated. By a similar method, the liquid composition ($x_1$, $x_2$, $x_3$) is obtained. Additionally, because similar system lines are used for sampling from two phases, when the six-port valve is switched for sampling from another phase the fluid from the cell should be kept flowing without sampling for about 1 to 2 min to avoid the carryover of the samples. Another key point is to ensure that the sample is taken from an equilibrium system by sampling only when the liquid−gas interface is clearly visible.

The structure of our apparatus avoided pressure fluctuation during the equilibrium and sampling steps because the equilibrium cell pressure was maintained at the set values (the required values) by setting the ISCO pump in the mode of constant pressure. More importantly, during sampling, the $CO_2$ flow rate should be kept relatively low by adjusting the BPR microswitch. In our experiment, the $CO_2$ flow rate was maintained at less than 20 $mL \cdot min^{-1}$ and 5 $mL \cdot min^{-1}$ (at 0.1 MPa and room temperature) during sampling from gas and liquid, respectively.

To obtain more accurate results, all data represent mean values of three samplings at uniform conditions with an uncertainty of ±0.001 mass fraction for gas composition and ±0.002 for liquid composition, respectively.

For gas-phase sampling, the amount of $CO_2$ was adjusted to be about 2 L (at 0.1 MPa and room temperature) at experimental pressures lower than 20 MPa because low solubility at low pressure was a main reason for experimental error; however, for higher pressures ($\geqslant$20 MPa), the amount of $CO_2$ was about 1 L (at 0.1 MPa and room temperature). For the liquid phase, the amount of $CO_2$ was adjusted to be about 0.01 to 0.02 L (at 0.1 MPa and room temperature). The methyl oleate and tocopherol content in the liquid sample was generally high and required dilution before chromatographic analysis.

***Analysis Methods.*** The samples dissolved in *n*-hexane were analyzed by GC to determine the concentration of methyl oleate. An analysis of tocopherol was performed by HPLC.[4]

***Correlation for Experimental Data.*** The Soave−Redlich−Kwong (SRK) EOS[5] in combination with the Adachi−Sugie (AS)[6] mixing rule was used to correlate the experimental data. In total, there were three binary interaction parameters ($k_{ij}$, $l_{ij}$, $\lambda_{ij}$) employed in the simulation. This procedure of correlation was completed with PE 2000, developed by Pfohl, Petkov, and Brunner.[7] A similar method was successfully applied for correlating the binary phase equilibria of $CO_2$ + methyl oleate and $CO_2$ + α-tocopherol.[4]

The deviation between experimental and correlated values was defined by

$$\Delta\xi = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\xi_i^{\text{exptl}} - \xi_i^{\text{calcd}}}{\xi_i^{\text{exptl}}}\right)^2} \qquad (1)$$

where $\xi_i$ is the mass fraction of component *i*.

***Separation Factor (S) between Tocopherol (Compound 2) and Methyl Oleate (Compound 1).*** According to the measured gas and liquid composition data, the separation factor ($S$) between tocopherol and methyl oleate was calculated by

$$S = \frac{y_2/x_2}{y_1/x_1} \qquad (2)$$

The separation factor represents the process selectivity for separating methyl oleate from tocopherol. In detail, a lower value indicates higher selectivity, whereas a higher value indicates that it is more difficult to separate the two compounds under certain conditions. Furthermore, when the separation factor equals unity, the composition in the gas phase is similar to that in the liquid, and the supercritical $CO_2$ process cannot separate methyl oleate from tocopherol.

***Experimental Ranges.*** In this work, we investigated the influences of three factors on phase behavior: pressure (from 10 to 29 MPa), temperature (from 313.15 to 353.15 K), and initial feed composition. Six initial feed compositions (0, 10.19, 32.44, 50.46, 71.93, and 100 mass %) were investigated. Among these, 0 and 100% stood for the pure compositions of methyl oleate and α-tocopherol, respectively. Their corresponding phase equilibrium data were cited from our previous research on binary systems.[4] The feed composition of ME-DOD was 10.19%. Other feed compositions were prepared by mass with an electric scale accurate to within $\pm 10^{-4}$ g.

**Table 1. Phase Equilibrium Data for the Ternary System Methyl Oleate (1) + Tocopherol (2) + $CO_2$ (3) at $T$ = 313.15 K**

| | | gas composition | | liquid composition | | |
|---|---|---|---|---|---|---|
| $p$/MPa | feed | $y_1$ | $y_3$ | $x_1$ | $x_3$ | $S$ |
| 10 | 0.0000 | 0.0301 | 0.9699 | 0.3811 | 0.6189 | |
| | 0.1019 | 0.0165 | 0.9831 | 0.4137 | 0.5201 | 0.1515 |
| | 0.3244 | 0.0099 | 0.9895 | 0.3193 | 0.4588 | 0.0872 |
| | 0.5046 | 0.0048 | 0.9944 | 0.2447 | 0.3526 | 0.1013 |
| | 0.7193 | 0.0025 | 0.9965 | 0.1711 | 0.2224 | 0.1128 |
| | 1.0000 | 0.0000 | 0.9983 | 0.0000 | 0.2251 | |
| 15 | 0.1019 | 0.0911 | 0.9050 | 0.3396 | 0.5829 | 0.1876 |
| | 0.3244 | 0.0398 | 0.9557 | 0.2759 | 0.5143 | 0.1487 |
| | 0.5046 | 0.0191 | 0.9768 | 0.2026 | 0.4245 | 0.1166 |
| | 0.7193 | 0.0118 | 0.9826 | 0.1489 | 0.2630 | 0.1202 |
| | 1.0000 | 0.0000 | 0.9928 | 0.0000 | 0.2424 | |
| 20 | 0.1019 | 0.1261 | 0.8630 | 0.2611 | 0.6752 | 0.3543 |
| | 0.3244 | 0.0665 | 0.9236 | 0.2250 | 0.5849 | 0.1762 |
| | 0.5046 | 0.0310 | 0.9586 | 0.1639 | 0.4877 | 0.1578 |
| | 0.7193 | 0.0203 | 0.9682 | 0.1284 | 0.3024 | 0.1278 |
| | 1.0000 | 0.0000 | 0.9886 | 0.0000 | 0.2554 | |
| 25 | 0.1019 | 0.1605 | 0.8226 | 0.2105 | 0.7301 | 0.3731 |
| | 0.3244 | 0.0851 | 0.8985 | 0.1640 | 0.6895 | 0.2157 |
| | 0.5046 | 0.0418 | 0.9418 | 0.1293 | 0.5660 | 0.1665 |
| | 0.7193 | 0.0227 | 0.9608 | 0.1007 | 0.3625 | 0.1364 |
| | 1.0000 | 0.0000 | 0.9822 | 0.0000 | 0.2579 | |
| 29 | 0.3244 | 0.0862 | 0.8857 | 0.1323 | 0.7283 | 0.3094 |
| | 0.5046 | 0.0558 | 0.9163 | 0.1048 | 0.6089 | 0.1830 |
| | 0.7193 | 0.0263 | 0.9479 | 0.0774 | 0.3952 | 0.1440 |
| | 1.0000 | 0.0000 | 0.9777 | 0.0000 | 0.2642 | |

## Results and Discussion

The isotherms at 313.15, 333.15, and 353.15 K for the ternary system of methyl oleate (1) + tocopherol (2) + $CO_2$ (3) were measured over the pressure range from 10 to 29 MPa. The experimental results are shown in Tables 1, 2, and 3.

***Influences of Pressure and Temperature on Phase Equilibrium.*** At 313.15 K, the composition data at 10, 20, and 29 MPa are drawn in a triangular diagram, as shown in Figure 2. Obviously, the two-phase region, which is surrounded by the equilibrium data, shrinks with increasing pressure. In other words, the mutual solubility of the components is increased. Figure 2a shows that the $CO_2$ mass fraction in the liquid rises with increasing pressure, whereas the $CO_2$ mass fraction in the gas is reduced, as shown in Figure 2b, which means that the solubilities of other components in the gas increase. At lower pressures (10 MPa), because both methyl oleate and tocopherol have limited miscibility in $CO_2$, the ternary phase behavior reveals a phase equilibrium of ternary type II;[8] thus, there is no critical point. At higher pressures (20, 29 MPa), because methyl oleate and $CO_2$ are completely miscible, the two-phase area is of ternary type I, which is characterized by a critical point, where the two phases become identical. In the type I system, higher solubilities in the gas can be reached than in the ternary type II system.

In addition to the measured data, Figure 2 shows the tie lines connecting the equilibrium data in the liquid and gas phases. The tie lines were correlated with the SRK EOS and the AS mixing rule. Characteristically, the gradient of the equilibrium tie lines gradually changes from one side line of the triangle to the other. This means that with increasing methyl oleate mass fraction in the feed the phase behavior tends to be close to that of the binary system of methyl oleate + $CO_2$.

In our previous research on the binary systems of $CO_2$ + methyl oleate and $CO_2$ + α-tocopherol, a series of binary interaction parameters were obtained, but we failed to apply them directly in correlating the ternary data of

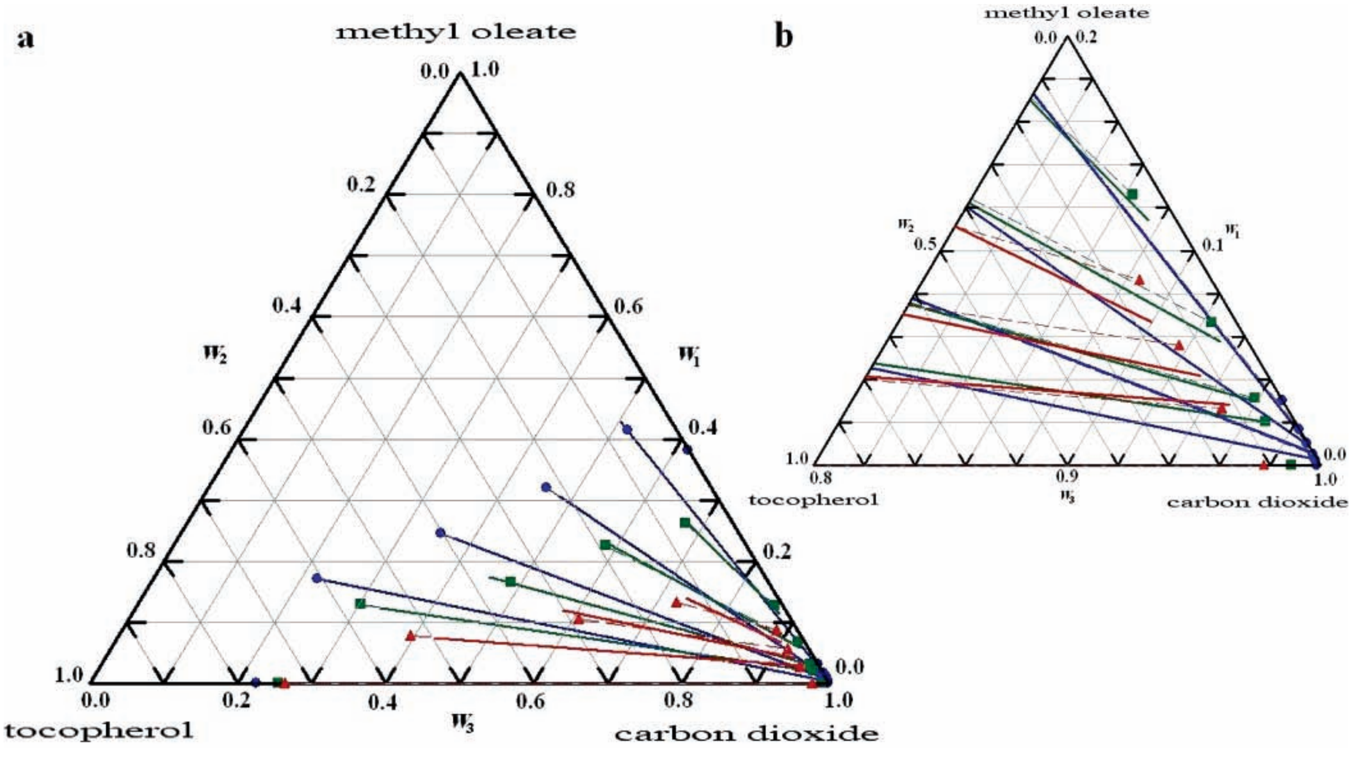

**Figure 2.** Influence of pressure on the phase equilibria of ($w_1$ methyl oleate + $w_2$ tocopherol + $w_3$ $CO_2$) at $T$ = 313.15 K: (a) liquid−gas equilibria; (b) equilibrium compositions in the gas; ●, experimental data at $p$ = 10 MPa; ■, experimental data at $p$ = 20 MPa; ▲, experimental data at $p$ = 29 MPa; blue line, correlated tie lines at $p$ = 10 MPa; green line, correlated tie lines at $p$ = 20 MPa; red line, correlated tie lines at $p$ = 29 MPa.

**Table 2. Phase Equilibrium Data for the Ternary System Methyl Oleate (1) + Tocopherol (2) + $CO_2$ (3) at $T$ = 333.15 K**

| | | gas composition | | liquid composition | | |
|---|---|---|---|---|---|---|
| $p$/MPa | feed | $y_1$ | $y_3$ | $x_1$ | $x_3$ | $S$ |
| 10 | 0.0000 | 0.0029 | 0.9971 | 0.6532 | 0.3468 | |
| | 0.1019 | 0.0029 | 0.9970 | 0.5882 | 0.3286 | 0.1193 |
| | 0.3244 | 0.0030 | 0.9969 | 0.4028 | 0.3428 | 0.0660 |
| | 0.5046 | 0.0025 | 0.9972 | 0.2813 | 0.3139 | 0.0818 |
| | 0.7193 | 0.0020 | 0.9973 | 0.1822 | 0.2502 | 0.1124 |
| | 1.0000 | 0.0000 | 0.9985 | 0.0000 | 0.2169 | |
| 20 | 0.1019 | 0.1417 | 0.8497 | 0.2904 | 0.6506 | 0.2987 |
| | 0.3244 | 0.0671 | 0.9255 | 0.2582 | 0.5454 | 0.1450 |
| | 0.5046 | 0.0368 | 0.9557 | 0.1996 | 0.4455 | 0.1146 |
| | 0.7193 | 0.0163 | 0.9760 | 0.1338 | 0.3311 | 0.1181 |
| | 1.0000 | 0.0000 | 0.9894 | 0.0000 | 0.2544 | |
| 29 | 0.3244 | 0.0956 | 0.8827 | 0.1739 | 0.6688 | 0.2509 |
| | 0.5046 | 0.0593 | 0.9184 | 0.1404 | 0.5641 | 0.1787 |
| | 0.7193 | 0.0312 | 0.9472 | 0.1093 | 0.3647 | 0.1439 |
| | 1.0000 | 0.0000 | 0.9798 | 0.0000 | 0.2624 | |

**Table 3. Phase Equilibrium Data for the Ternary System Methyl Oleate (1) + Tocopherol (2) + $CO_2$ (3) at $T$ = 353.15 K**

| | | gas composition | | liquid composition | | |
|---|---|---|---|---|---|---|
| $p$/MPa | feed | $y_1$ | $y_3$ | $x_1$ | $x_3$ | $S$ |
| 10 | 0.0000 | 0.0028 | 0.9972 | 0.7439 | 0.2561 | |
| | 0.1019 | 0.0027 | 0.9972 | 0.6905 | 0.2285 | 0.0838 |
| | 0.3244 | 0.0025 | 0.9974 | 0.4324 | 0.2347 | 0.0708 |
| | 0.5046 | 0.0023 | 0.9975 | 0.2855 | 0.2486 | 0.0681 |
| | 0.7193 | 0.0019 | 0.9975 | 0.1470 | 0.2221 | 0.0736 |
| | 1.0000 | 0.0000 | 0.9986 | 0.0000 | 0.2194 | |
| 20 | 0.0000 | 0.0829 | 0.9171 | 0.3343 | 0.6657 | |
| | 0.1019 | 0.066 | 0.9303 | 0.3416 | 0.5757 | 0.2065 |
| | 0.3244 | 0.0438 | 0.9502 | 0.2772 | 0.4488 | 0.1386 |
| | 0.5046 | 0.0231 | 0.9717 | 0.2152 | 0.3595 | 0.1139 |
| | 0.7193 | 0.0085 | 0.9868 | 0.1164 | 0.2728 | 0.1054 |
| | 1.0000 | 0.0000 | 0.9941 | 0.0000 | 0.2554 | |
| 29 | 0.3244 | 0.0628 | 0.9204 | 0.1572 | 0.6567 | 0.2260 |
| | 0.5046 | 0.0444 | 0.9374 | 0.1313 | 0.5392 | 0.1633 |
| | 0.7193 | 0.0200 | 0.9638 | 0.0795 | 0.3372 | 0.1104 |
| | 1.0000 | 0.0000 | 0.9836 | 0.0000 | 0.3320 | |

methyl oleate (1) + tocopherol (2) + $CO_2$ (3). Consequently, we perused literature concerning methyl oleate + squalene + $CO_2$ [9] and fish oil ethyl esters + $CO_2$,[10] which were, more or less, similar to the system in this work. We adopted their method for estimating interaction parameters. First, the initial values for two interaction parameters ($k_{ij}$, $l_{ij}$) were found by iteration in the range of −1 to 1 while $\lambda_{ij}$ was kept to be zero, and then all interaction parameters ($k_{ij}$, $l_{ij}$, $\lambda_{ij}$) were optimized by fitting the EOS to experimentally determined $pTxy$ data until the deviations ($\Delta\zeta$) between the calculated and experimental data (eq 1) were minimized to be lower than 15%. Table 4 lists the optimized binary interaction parameters and correlation deviations for the experimental data shown in Figures 2 and 3.

Figure 3 shows the influence of temperature on phase equilibrium at 20 MPa. Obviously, the influence of temperature is contrary to that of pressure. With increasing temperature, the two-phase area expands, as shown in Figure 3a. In addition, the phase equilibria are of ternary type I at 313.15 and 333.15 K, and then at 353.15 K the phase equilibrium develops into ternary type II; here the binary critical pressure for $CO_2$ + methyl oleate is greater than 20 MPa. Noticeably, the influence of temperature on the gas composition seems to be less significant than that on the liquid composition at 20 MPa, as shown in Figure 3b.

***Separation Factor between Tocopherol and Methyl Oleate.*** Utilizing eq 2 and the measured data, we calculated the separation factor between tocopherol and methyl oleate. Figures 4 and 5 show the influences of pressure and temperature on the separation factor, respectively.

In Figure 4, both the experimental data and correlated curve illustrate that at a constant temperature the separation factor increases as pressure increase, except for one part at 10 MPa. However, as shown in Figure 5, the influence of temperature is contrary to that of pressure. As mentioned above, a lower separation factor indicates a higher selectivity; accordingly, the tendencies shown in Figures 4 and 5 indicate that low pressure and high temperature lead to high selectivity, which is advantageous for separating methyl oleate from tocopherol with supercritical $CO_2$. In addition, at constant pressure and temperature, the separation factor increases as the initial tocopherol content ($x_2^0$) decreases. Moreover, this tendency is more obvious as pressure increases. A lower content of tocopherol means a higher content of methyl oleate because the feed mainly consisted of methyl oleate and tocopherol, among which the former is more soluble in supercritical $CO_2$. Consequently, more methyl oleate in the feed generates more tocopherol for distribution in supercritical $CO_2$, resulting in an increase in the separation factor. In other words, methyl oleate acts as the cosolvent for tocopherol. A similar phenomenon was also reported by Bamberger et al.,[11] who measured the solubilities of fatty acids, pure triglycerides, and triglyceride mixtures in supercritical $CO_2$. They found that the solubilities of the less soluble triglycerides in mixtures such as tripalmitin were enhanced by the presence of more soluble triglycerides such as trilaurin. In this situation, the more soluble compounds were said to act as the cosolvent.

***Equilibrium Lines.*** Using the obtained equilibrium data, we drew the equilibrium lines in the pressure and temperature ranges investigated. Figures 6 and 7 illustrate the equilibrium lines at 313 K and 20 MPa, respectively. The data were represented as the mass fraction of methyl oleate ($CO_2$-free basis).

As shown in the Figures, either a pressure increase or a temperature decrease moves the equilibrium line closer to the diagonal line. In fractionation designing, this tendency means that an increase in theoretical stages is accompanied by a decrease in process selectivity. Such a tendency agrees well with that illustrated by the separation factor.

To determine the number of theoretical stages for a certain separation requirement, we recognize that the

**Table 4. Correlation Deviation ($\Delta\zeta$/%) Obtained with SRK EOS and the AS Mixing Rule**

| | | optimized binary interaction parameters | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$/K | $p$/MPa | $k_{12}$ | $l_{12}$ | $\lambda_{12}$ | $k_{13}$ | $l_{13}$ | $\lambda_{13}$ | $k_{23}$ | $l_{23}$ | $\lambda_{23}$ | $\Delta\zeta$/% |
| 313.15 | 10 | −0.1712 | −0.3938 | 0.9589 | 0.2819 | 0.1771 | 0.1226 | 0.4151 | 0.0440 | 0.3054 | 9.1372 |
| | 20 | −0.1341 | −0.6964 | 0.5790 | 0.5441 | 0.1549 | 0.3733 | 0.5050 | 0.0134 | 0.3458 | 6.9603 |
| | 29 | −0.1394 | −0.9451 | 0.8600 | 0.3163 | 0.1685 | 0.1739 | 0.3189 | 0.0709 | 0.1835 | 12.2165 |
| 333.15 | 20 | −0.0982 | −0.4653 | 0.4265 | 0.5823 | 0.1962 | 0.4096 | 0.5325 | 0.0959 | 0.3633 | 2.3431 |
| 353.15 | 20 | −0.1716 | −0.5681 | 0.4172 | 0.5878 | 0.1342 | 0.4274 | 0.5071 | 0.0231 | 0.3419 | 7.9555 |

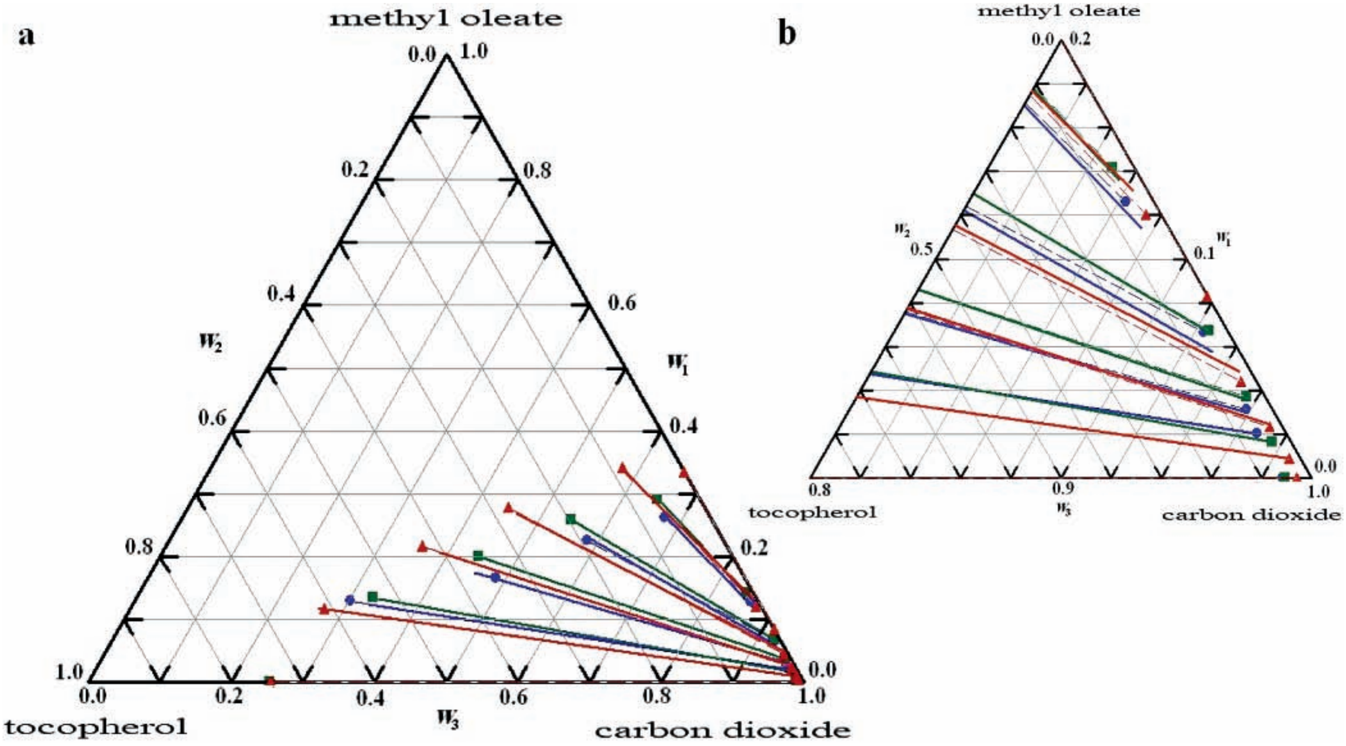

**Figure 3.** Influence of temperature on the phase equilibria of ($w_1$ methyl oleate + $w_2$ tocopherol + $w_3$ $CO_2$) at $p$ = 20 MPa: (a) liquid−gas equilibria; (b) equilibrium compositions in the gas; ●, experimental data at $T$ = 313.15 K; ■, experimental data at $T$ = 333.15 K; ▲, experimental data at $T$ = 353.15 K; blue line, correlated tie lines at $T$ = 313.15 K; green line, correlated tie lines at $T$ = 333.15 K; red line, correlated tie lines at $T$ = 353.15 K.

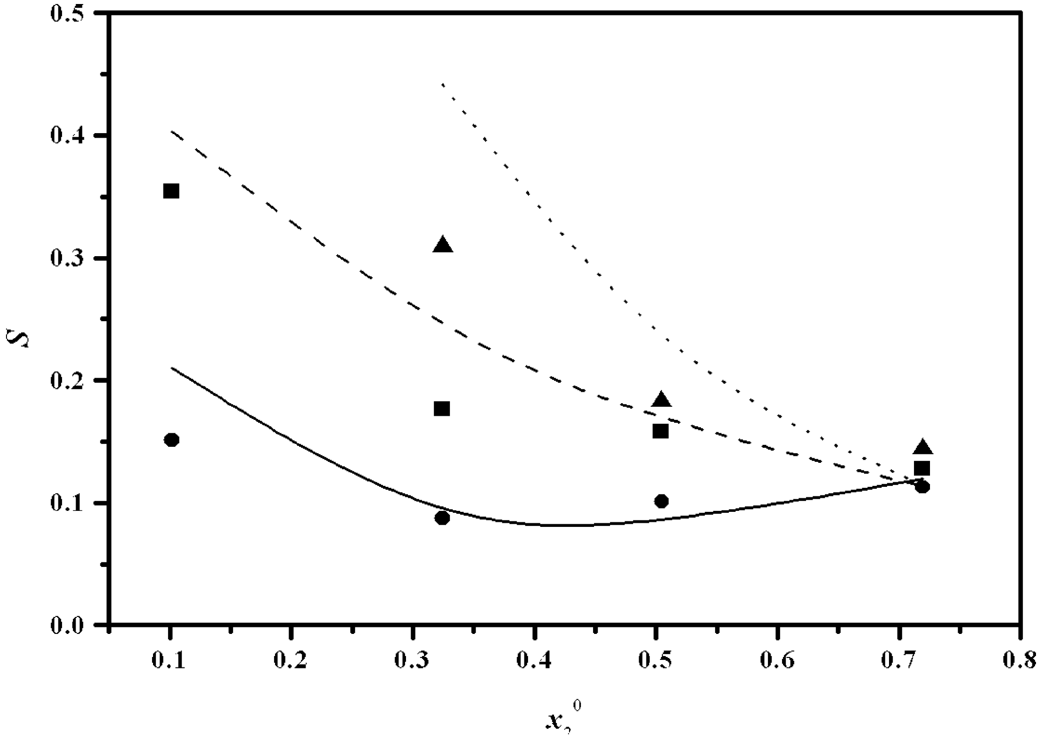

**Figure 4.** Influence of pressure on the separation factor ($S$) at $T$ = 313.15 K: $x_2^0$, initial tocopherol mass fraction in the feed; ▲, experimental data at $p$ = 29 MPa; ■, experimental data at $p$ = 20 MPa; ●, experimental data at $p$ = 10 MPa; ···, correlated at $p$ = 29 MPa; - - -, correlated at $p$ = 20 MPa; —, correlated at $p$ = 10 MPa.

equilibrium lines and the operation lines are the two significant preconditions.[8] The research on phase equilibrium helped us to obtain the equilibrium lines. As the next step, a series of fractionation experiments need to be carried out to determine the operation lines.

***Phase Behavior of ME-DOD.*** During the measurement of phase equilibrium, the realistic system of ME-DOD was taken as the 10.19% (tocopherol mass fraction) feed composition. Also, the ME-DOD system supplied the raw materials for concentrating natural tocopherols; thus, its

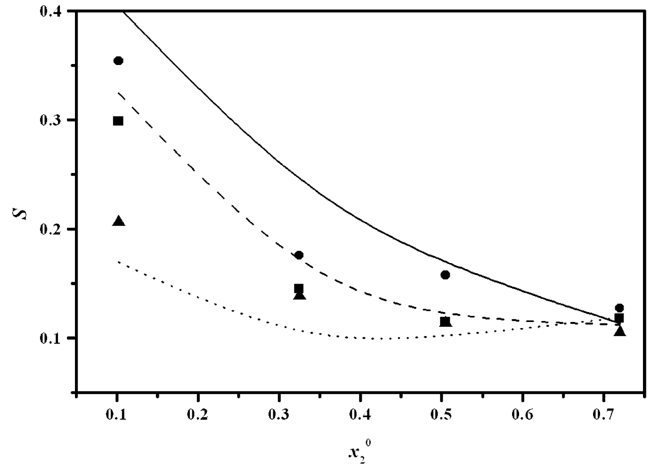

**Figure 5.** Influence of temperature on the separation factor ($S$) at $p = 20$ MPa: $x_2^0$, initial tocopherol mass fraction in the feed; ●, experimental data at $T = 313.15$ K; ■, experimental data at $T = 333.15$ K; ▲, experimental data at $T = 353.15$ K; —, correlated at $T = 313.15$ K; - - -, correlated at $T = 333.15$ K; ···, correlated at $T = 353.15$ K.

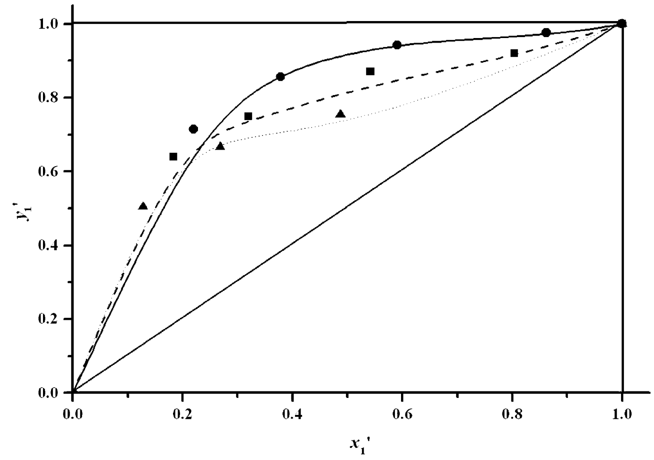

**Figure 6.** Equilibrium lines at $T = 313.15$ K: $x_1'$, mass fraction of methyl oleate in the liquid ($CO_2$-free basis); $y_1'$, mass fraction of methyl oleate in the gas ($CO_2$-free basis); ●, experimental data at $p = 10$ MPa; ■, experimental data at $p = 20$ MPa; ▲, experimental data $p = 29$ MPa; —, correlated at $p = 10$ MPa; - - -, correlated at $p = 20$ MPa; ···, correlated at $p = 29$ MPa.

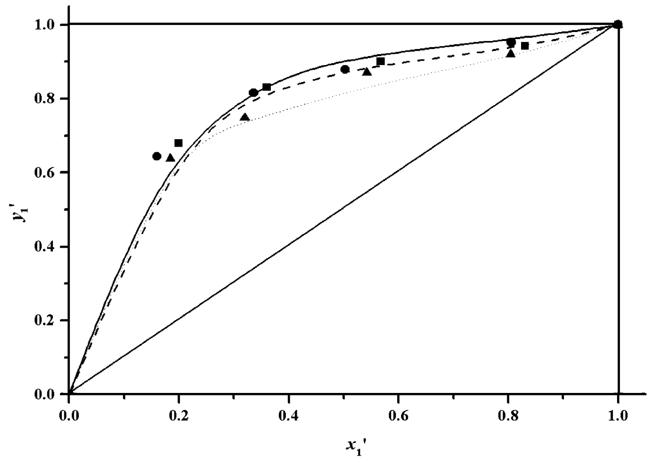

**Figure 7.** Equilibrium lines at $p = 20$ MPa: $x_1'$, mass fraction of methyl oleate in the liquid ($CO_2$-free basis); $y_1'$, mass fraction of methyl oleate in the gas ($CO_2$-free basis); ●, experimental data at $T = 353.15$ K; ■, experimental data at $T = 333.15$ K; ▲, experimental data $T = 313.15$ K; —, correlated at $T = 353.15$ K; - - -, correlated at $T = 333.15$ K; ···, correlated at $T = 313.15$ K.

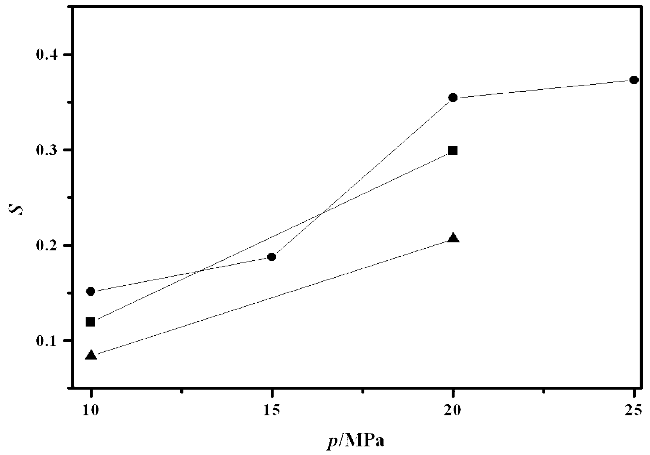

**Figure 8.** Separation factor ($S$) of ME-DOD in supercritical $CO_2$: ●, experimental data at $T = 313.15$ K; ■, experimental data at $T = 333.15$ K; ▲, experimental data $T = 353.15$ K.

phase behavior is separately discussed. Figure 8 shows the influence of pressure and temperature on the separation factor.

The trends illustrated in Figure 8 are similar to those in Figures 4 and 5. Noticeably, the separation factors at pressures lower than 20 MPa are relatively small. For instance, at 313.15 K, the separation factor remained lower than 0.2 for all pressures lower than 15 MPa. As pressure increases, the separation factor increases greatly, reaching 0.3542 at 20 MPa. The increase in temperature offsets the effect of pressure to some extent. On the basis of this property, a separation strategy seems to be reasonable and feasible. A fractionation column is necessary for the ME-DOD liquid system. First, low pressure (15 to 20 MPa) was used in combination with a temperature distribution in the column to separate methyl oleate. Then, the pressure was increased to separate tocopherol from other impurities. This procedure needs to be verified by a fractionation operation in which operation parameters can be determined and optimized.

During our experiments, some phenomena of the realistic system of ME-DOD + $CO_2$ were observed through the visual equilibrium cell. Figure 9 shows the liquid−gas interface changes that occur as pressure is increased. The interface increasingly changes from clear to obscure, with the interface finally disappearing at high pressure of about 29 MPa. At high pressure, a critical point probably exists that causes the whole system to become entirely miscible. In this situation, the liquid and gas compositions are identical, and the separation factor equals unity. It should be noticed that the disappearance of the interface does not happen suddenly. The change is a progressive process, and the endpoint is difficult to determine accurately by visual observation. The critical pressure at 313.15 K is estimated in the pressure range from 27.8 to 29.0 MPa by visual observation.

Figure 10 shows the changes in the feed situation when the equilibrium cell was charged with ME-DOD via pump at different pressures and at a constant 5 mL·min$^{-1}$. At low pressure (5 MPa), ME-DOD could smoothly flow into the equilibrium cell, but at high pressure, the charged ME--

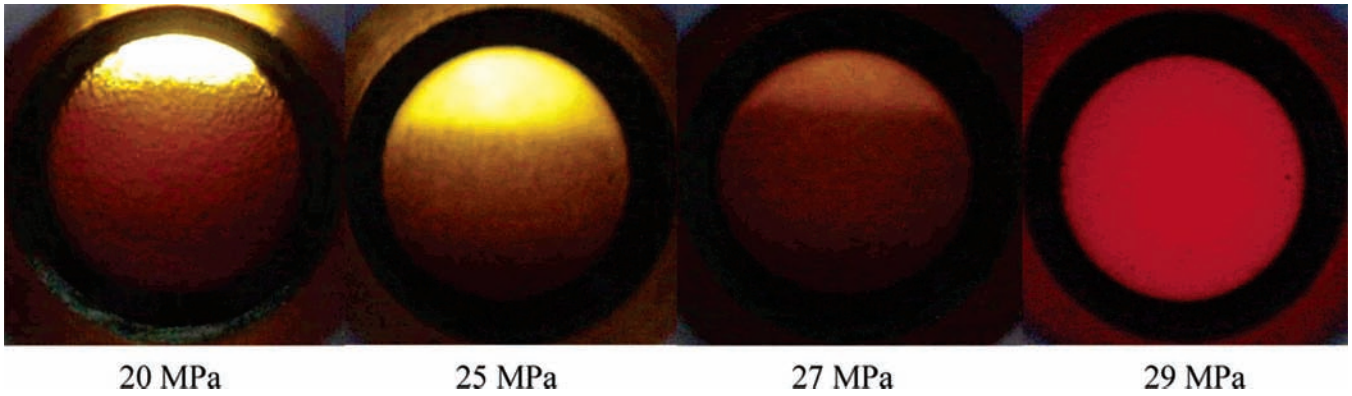

**Figure 9.** Interface between liquid and gas at $T = 313.15$ K.

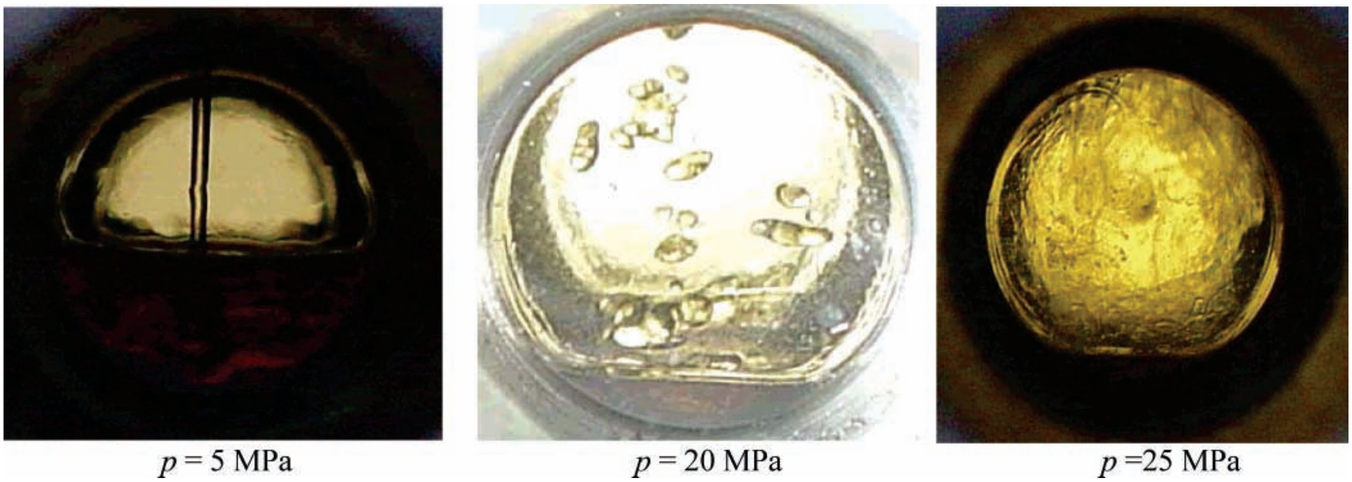

**Figure 10.** Feed situation of ME-DOD at different pressures (feed rate = 5 mL·min$^{-1}$ and $T = 313.15$ K).

DOD resembles drops or fog. Moreover, the rate for flowing downward at a high pressure was slower than at low pressure. We hypothesized that the main reason was the smaller difference in density between ME-DOD and supercritical $CO_2$ at high pressure; for example, at 20 MPa and 313.15 K, the density of $CO_2$ is 0.840 g·mL$^{-1}$, and that of ME-DOD is 0.865 g·mL$^{-1}$. Such a small difference in density likely caused the drop or fog phenomenon, even though the clear interface between liquid and gas remained. This phenomenon should be considered when designing a continuously countercurrent operation.

## Conclusions

In this work, phase equilibrium data of methyl oleate (1) + tocopherol (2) + $CO_2$ (3) were measured and correlated with the Soave−Redlich−Kwong EOS and Adachi−Sugie mixing rule. On the basis of the experimental data and correlation results, the separation factor and equilibrium line were investigated. The discussion indicated that lower pressures and higher temperatures lead to a higher selectivity. Also, a higher content of methyl oleate in the feed improved the distribution of tocopherols in gas, resulting in a decrease in selectivity. In addition, the experimental data on ME-DOD helped to form a preliminary separation strategy, which must be tested through a supercritical $CO_2$ fractionation operation. Finally, the visual observations of ME-DOD also provided some valuable information for further experimentation and design.

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