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# High-Pressure Phase Behavior of Binary Mixtures of Octafluoropentyl Acrylate and Octafluoropentyl Methacrylate in Supercritical Carbon Dioxide

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**ABSTRACT:** Pressure−composition isotherms are obtained for the carbon dioxide + 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (OFPA) and carbon dioxide + 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA) systems using a static apparatus at a temperature range from (313.2 to 393.2) K and pressures up to 17.86 MPa. The solubility of OFPA and OFPMA for the (carbon dioxide + OFPA) and (carbon dioxide + OFPMA) systems increases as the temperature increases at constant pressure. Liquid−liquid−vapor equilibria for the (carbon dioxide + OFPA) and (carbon dioxide + OFPMA) systems were not observed at these conditions. We determined new parameters for the critical constants by using the Joback, modified Joback, and Constantinou−Gani group contribution methods. The acentric factor was determined by using Ambrose and Walton's method. Using these parameters, the experimental results for (carbon dioxide + OFPA) and (carbon dioxide + OFPMA) systems are correlated with the Peng−Robinson equation of state (EOS) using a van der Waals one-fluid mixing rule including two adjustable parameters. We compared the three Joback, modified Joback, and Constantinou−Gani group contribution methods.

## 1. INTRODUCTION

Perfluoro(meth)acrylate monomers are hydrophobic, which impart solubility and wetting properties for adhesion and pigment transportation.[1] Therefore, information on phase behavior for perfluoro(meth)acrylate containing supercritical carbon dioxide is required for practical use. 2,2,3,3,4,4,5,5-Octafluoropentyl acrylate (OFPA) and 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA) are low volatility, monofunctional, aromatic monomers that offer good adhesion properties.

Recently, phase behavior experiments have been reported on the bubble-point, dew-point, and critical-point behavior of (meth)-acrylate monomers containing supercritical carbon dioxide.[2,3] Supercritical carbon dioxide used in this work is widely used as an environmentally benign solvent which is inexpensive, nonflammable, and nontoxic. Particularly, supercritical carbon dioxide has a quadrupole moment, no dipole moment, and a low dielectric constant. Supercritical carbon dioxide is a good solvent with low molecular weight in nonpolar molecules.

Desimone et al. reported the first successful homogeneous free radical polymerization of fluoropolymers in supercritical carbon dioxide.[4] The phase behavior for the binary mixture of the perfluoro(meth)acrylate with supercritical carbon dioxide plays an important role in the fluoropolymer processes, polymerization optimum conditions, and various industrial applications including textile finishes, resists, protective coatings, charge control agents, optical fibers, contact lenses, and so forth.[5,6]

In this work, the measurement is aimed at obtaining the phase equilibrium data for (carbon dioxide + OFPA) and (carbon dioxide + OFPMA) mixtures by investigating mixtures of carbon dioxide with two components using a variable volume view cell at temperatures from (313.2 to 393.2 K) and pressures up to 17.86 MPa. Also, the pressure−composition ($P-x$) diagrams of the mixture critical curve are presented for the (carbon dioxide + OFPA) and (carbon dioxide + OFPMA) systems at each of the five temperatures. The experimental data for (carbon dioxide + OFPA) and (carbon dioxide + OFPMA) systems obtained in this work are correlated with the Peng−Robinson equation of state (EOS)[7,8] using a van der Waals one-fluid mixing rules including two adjustable parameters. The properties of critical pressure and critical temperature of OFPA and OFPMA are reported in the calculated data by the Joback, modified Joback and Constantinou−Gani group contribution methods,[9,10] while the vapor pressure is estimated by the Lee−Kesler method.[11] The acentric factor was determined by Ambrose and Walton.[9] Using these pure parameters, we compared the three Joback, modified Joback, and Constantinou−Gani group contribution methods.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Carbon dioxide (min. 99.8 %) was purchased from Daesung Industrial Gases. 2,2,3,3,4,4,5,5-Octafluoropentyl acrylate (OFPA) [97 % purity, CAS Registry No. 376-84-1] and 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA) [98 % purity, CAS Registry No. 355-93-1] were obtained from Alfa Aeser Co. and used without further purification. They contained 4-methoxyphenol as an inhibitor to prevent polymerization. The concentration of 4-methoxyphenol was 50 ppm for the amount of perfluoro monomer. The molecular structures of OFPA and OFPMA monomers used in experiments are shown in Figure 1.

**2.2. Apparatus and Procedures.** Figure 2 shows a schematic diagram of the static-type apparatus containing a variable-volume view cell to obtain high-pressure phase behavior data.[11] The main components of the experimental apparatus are a high-pressure generator, an air bath (with a variable-volume view cell), and a

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visual part. The high-pressure generator (HIP Co., model 37-5.75-60) is controlled to the desired operating pressure using pressed water. The mixture in the view cell was compressed to the desired pressure by moving a piston (2.54 cm length) located with the cell. A small correction (0.05 MPa) was added to account for the pressure required to move the piston. The pressure of mixture is measured with a Heise gauge (Dresser Ind., model CM-53920, (0 to 34.0) MPa) accurate to ± 0.02 MPa.

The air bath is controlled at a constant temperature in a variable-volume view cell. This view cell is constructed of high nickel content austenitic steel (5.7 cm outer diameter, 1.59 cm inner diameter, about 28 $cm^3$ working volume, fitted with a 1.9 cm outer diameter, 1.3 cm thick sapphire window). A magnetic stir bar in the cell helped the mixture to reach equilibrium. The temperature of the cell was maintained to within ± 0.1 K and measured to within ± 0.1 K.

The visual status of the inside was projected onto the monitor (M&J Technology Co., model HT-1900WT) using a camera (Watec Corp., model WAT-202B) with a boroscope (Olympus Corp., model R100-038-000-50) set toward the sapphire window.

The view cell was purged twice with $N_2$ gas and $CO_2$ at room temperature to remove traces of air and organic matter. The measured monomer was loaded in a view cell by using a syringe to within ± 0.001 g. $CO_2$ was added to the cell to within ± 0.002 g using a high-pressure bomb. The mixture could be compressed to the desired operating pressure by replacing a piston fitted within the cell using pressed water with a high-pressure generator.

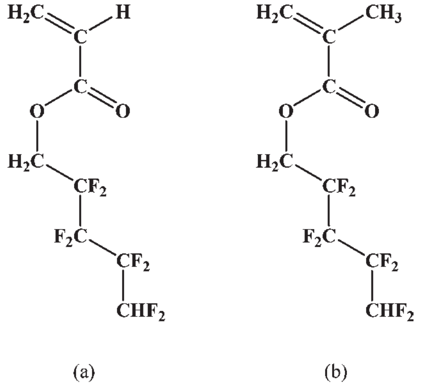

**Figure 1.** Chemical structure of two monomers: (a) 2,2,3,3,4,4,5,5-octafluoropentyl acrylate (OFPA) and (b) 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA).

At a fixed temperature, the mixture in the cell was compressed to a single phase at high pressures. The pressure was then slowly decreased until a second phase (bubble, mixture critical, or dew point) appeared. Critical points were obtained by adjusting the temperature and pressure of the mixture until critical opalescence was observed along with equal liquid and vapor volume upon formation of the second phase. A bubble-point pressure was obtained when small vapor bubbles appeared in the cell, while a dew point was obtained after a fine mist appeared.

Experimental data for the carbon dioxide + OFPA and carbon dioxide + OFPMA systems were measured, and the experimental uncertainty was estimated from ± 0.3 MPa to ± 0.5 MPa and ± 0.2 K for a given loading of the cell. The mole fractions are accurate to within ± 0.002.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

**3.1. Phase Equilibrium Data.** Figure 3, Table 1, and Table 2 show pressure—composition ($P-x$) isotherms for carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems at (313.2, 333.2, 353.2, 373.2, and 393.2) K and pressures up to 17.86 MPa. The carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems do not exhibit three phases at the five temperatures investigated.[12]

Figure 4 represents the comparison of carbon dioxide + OFPA (above) and carbon dioxide + pentyl acrylate (above) systems and that of carbon dioxide + OFPMA (bottom) and carbon dioxide + pentyl methacrylate (bottom) systems at 353.2 K. The curves of the $P-x$ isotherms are a similar shape, while in the case of OFPA and OFPMA, the phase behavior pressure (fluid → liquid + vapor) is slightly lower than the corresponding pentyl acrylate and pentyl methacrylate in the mixture critical-point region which has no fluorine in its molecular structure. However, the bubble-point behavior of carbon dioxide + OFPA and carbon dioxide + OFPMA systems at 353.2 K is slightly lower than carbon dioxide + pentyl acrylate and carbon dioxide + pentyl methacrylate systems above ca. 0.2 (mole fraction) at 353.2 K.

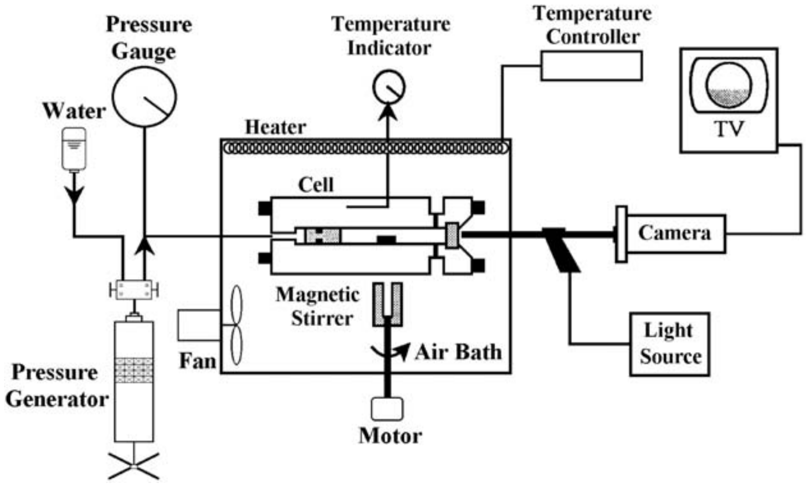

**Figure 2.** Schematic diagram of the experimental apparatus.

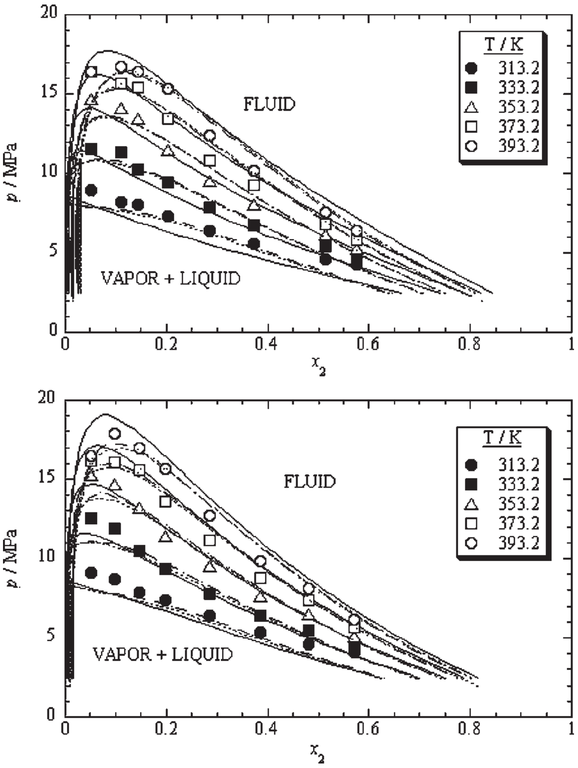

**Figure 3.** Comparison of the experimental data (symbols) for the carbon dioxide (1) + OFPA (2) (above) and carbon dioxide (1) + OFPMA (2) (bottom) systems with calculations obtained with the Peng–Robinson EOS among the Joback method (long dashed line), modified Joback method (short dashed line), and Conatantinou–Gani (C-G) method (solid line). ●, 313.2 K; ■, 333.2 K; △, 353.2 K; □, 373.2 K; ○, 393.2 K.

The substitution of hydrogen to fluorine in acrylate or methacrylate dramatically lowers the phase behavior pressure. This phenomenon is due to cross interaction between fluorine–(meth)acrylate and carbon dioxide. Below ca. 0.2 (mole fraction), the pressure difference in the mixture-critical point at 353.2 K of each system (carbon dioxide + OFPA and carbon dioxide + PnA systems; carbon dioxide + OFPMA and carbon dioxide + PnMA systems) is ca. 1.2 MPa (above) and ca. 2.0 MPa (bottom). This result comes from monomer + monomer self-interactions which are stronger than monomer + carbon dioxide cross interactions.

**3.2. Modeling of Experimental Data.** Experimental data obtained in this study were modeled with the Peng–Robinson EOS using the van der Waals one-fluid mixing rule including two binary interaction parameters ($k_{ij}$, $\eta_{ij}$). The Peng–Robinson equations are briefly described here. The Peng–Robinson EOS[7] was used with the following mixing rules:

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = (a_{ii}a_{jj})^{1/2}(1 - k_{ij})$$

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij}$$

$$b_{ij} = 0.5(b_{ii} + b_{jj})(1 - \eta_{ij})$$

**Table 1. Experimental Data for the Carbon Dioxide (1) + 2,2,3,3,4,4,5,5-Octafluoropentyl Acrylate (2) System**

| $x_2$ | $p$/MPa | transition[a] |
|---|---|---|
| | $T$ = 313.2 K | |
| 0.052 | 8.93 | BP |
| 0.109 | 8.17 | BP |
| 0.145 | 8.00 | BP |
| 0.203 | 7.28 | BP |
| 0.285 | 6.41 | BP |
| 0.373 | 5.59 | BP |
| 0.514 | 4.64 | BP |
| 0.575 | 4.29 | BP |
| | $T$ = 333.2 K | |
| 0.052 | 11.55 | BP |
| 0.109 | 11.35 | BP |
| 0.145 | 10.28 | BP |
| 0.203 | 9.45 | BP |
| 0.285 | 7.90 | BP |
| 0.373 | 6.72 | BP |
| 0.514 | 5.41 | BP |
| 0.575 | 4.82 | BP |
| | $T$ = 353.2 K | |
| 0.052 | 14.66 | BP |
| 0.109 | 14.10 | BP |
| 0.145 | 13.41 | BP |
| 0.203 | 11.48 | BP |
| 0.285 | 9.52 | BP |
| 0.373 | 8.04 | BP |
| 0.514 | 6.12 | BP |
| 0.575 | 5.28 | BP |
| | $T$ = 373.2 K | |
| 0.052 | 16.41 | BP |
| 0.109 | 15.69 | BP |
| 0.145 | 15.45 | BP |
| 0.203 | 13.48 | BP |
| 0.285 | 10.86 | BP |
| 0.373 | 9.28 | BP |
| 0.514 | 6.78 | BP |
| 0.575 | 5.79 | BP |
| | $T$ = 393.2 K | |
| 0.052 | 16.38 | DP |
| 0.109 | 16.73 | CP |
| 0.145 | 16.38 | BP |
| 0.203 | 15.35 | BP |
| 0.285 | 12.35 | BP |
| 0.373 | 10.17 | BP |
| 0.514 | 7.52 | BP |
| 0.575 | 6.38 | BP |

[a] BP is a bubble point, CP is a critical point, and DP is a dew point.

where $k_{ij}$ and $\eta_{ij}$ were binary interaction parameters determined by fitting ($P$, $x$) isotherm curves, and $a_{ii}$ and $b_{ii}$ were pure component parameters as defined by Peng and Robinson.[7]

The objection function (OBF) and root-mean-squared relative deviation percent [rmsd (%)] for this calculation were

**Table 2. Experimental Data for the Carbon Dioxide (1) + 2,2,3,3,4,4,5,5-Octafluoropentyl Methacrylate (2) System**

| $x_2$ | $p$/MPa | transition[a] |
|---|---|---|
| | $T$ = 313.2 K | |
| 0.051 | 9.14 | BP |
| 0.097 | 8.69 | BP |
| 0.147 | 7.90 | BP |
| 0.199 | 7.35 | BP |
| 0.285 | 6.38 | BP |
| 0.385 | 5.35 | BP |
| 0.480 | 4.59 | BP |
| 0.572 | 4.09 | BP |
| | $T$ = 333.2 K | |
| 0.051 | 12.52 | BP |
| 0.097 | 11.93 | BP |
| 0.147 | 10.52 | BP |
| 0.199 | 9.38 | BP |
| 0.285 | 7.79 | BP |
| 0.385 | 6.38 | BP |
| 0.480 | 5.48 | BP |
| 0.572 | 4.59 | BP |
| | $T$ = 353.2 K | |
| 0.051 | 15.28 | BP |
| 0.097 | 14.66 | BP |
| 0.147 | 13.17 | BP |
| 0.199 | 11.41 | BP |
| 0.285 | 9.48 | BP |
| 0.385 | 7.62 | BP |
| 0.480 | 6.45 | BP |
| 0.572 | 5.10 | BP |
| | $T$ = 373.2 K | |
| 0.051 | 16.17 | BP |
| 0.097 | 16.10 | BP |
| 0.147 | 15.57 | BP |
| 0.199 | 13.62 | BP |
| 0.285 | 11.17 | BP |
| 0.385 | 8.79 | BP |
| 0.480 | 7.35 | BP |
| 0.572 | 5.63 | BP |
| | $T$ = 393.2 K | |
| 0.051 | 16.52 | DP |
| 0.097 | 17.86 | CP |
| 0.147 | 16.97 | BP |
| 0.199 | 15.66 | BP |
| 0.285 | 12.72 | BP |
| 0.385 | 9.83 | BP |
| 0.480 | 8.10 | BP |
| 0.572 | 6.17 | BP |

[a] BP is a bubble point, CP is a critical point, and DP is a dew point.

defined by,

$$\mathrm{OBF} = \sum_{i}^{N} \left( \frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}} \right)^2 \qquad (1)$$

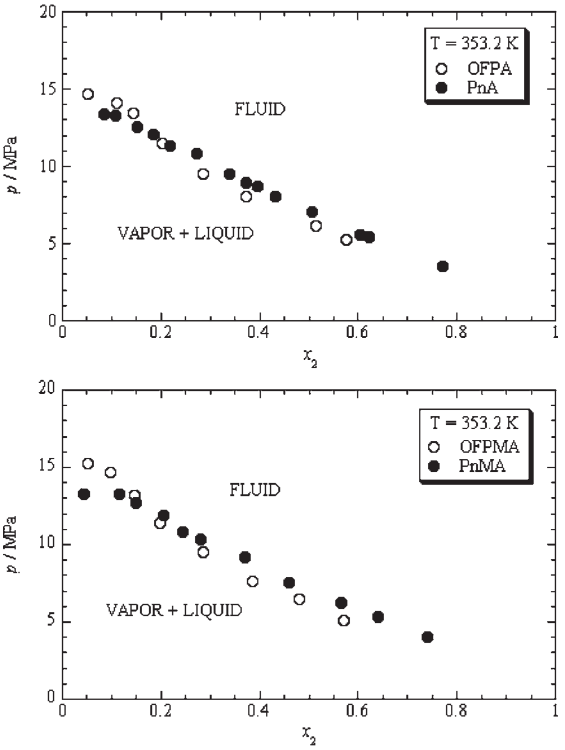

**Figure 4.** Comparison for the carbon dioxide (1) + OFPA (2) (above) with carbon dioxide (1) + *n*-pentyl acrylate[12] (2) system and the carbon dioxide (1) + OFPMA (2) (bottom) with carbon dioxide (1) + *n*-pentyl methacrylate[12] (2) system.

$$\mathrm{rmsd}(\%) = \sqrt{\left(\frac{\mathrm{OBF}}{\mathrm{ND}}\right)} \cdot 100 \qquad (2)$$

$P_{\mathrm{exp}}$ and $P_{\mathrm{cal}}$ are the experimental and calculated pressures, respectively. ND in eq 2 means the number of data points. To optimize the OBF, we used the Marquardt equation.[13] The critical temperature and pressure ($T_c$, $P_c$) and an acentric factor ($\omega$) are necessary to correlate experimental data with the Peng–Robinson EOS. The critical properties of OFPA and OFPMA were not reported in literature. We estimated the critical temperature and pressure ($T_c$, $P_c$) and acentric factor ($\omega$) with three different methods. The critical temperature and pressure were estimated with the Joback, modified Joback, and Constantinou–Gani group contribution methods, and the acentric factor ($\omega$) was estimated with the Ambrose–Walton method.[9] Table 3 shows the group contribution parameter for Joback (−F) and modified Joback (−F or $-\mathrm{CF_2}-$) group contribution method.[14,15] We need these parameters to obtain critical properties.

The calculation results of critical properties represented three different methods at Table 4. The Joback method was only considered for a simple fluorine fragment (−F). This method did not consider the more substituted cases (i.e., $-\mathrm{CF_2}-$). The modified Joback method was considered for fluorine fragments (−F and $-\mathrm{CF_2}-$).

Figure 5 compares the experimental data with the calculation results for the carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems among the Joback method (red dashed line), modified Joback method (blue dashed line),

**Table 3. Group Contribution Parameter for Joback and Modified Joback Method Parameters**

| group | $\Delta T_b$ | $\Delta T_c$ | $\Delta P_c$ | remarks |
|---|---|---|---|---|
| $-F$ | −0.03 | 0.0111 | −0.0057 | Joback group contribution method |
| $-F$ | 6.31[a] | 0.0111 | −0.0057 | modified Joback group contribution method |
| $-CF_2-$ | 20.17[a] | 0.0222[b] | −0.0036[b] | |

[a] Reference 14. [b] Reference 15.

**Table 4. Critical Constants and Acentric Factor of Pure Components[9]**

| component | $T_b$/K | $T_c$/K | $P_c$/bar | $\omega$ |
|---|---|---|---|---|
| carbon dioxide[a] | | 304.1 | 73.8 | 0.225 |
| OFPA[e] | 421.4[b] | 564.8[b] | 20.0[b] | 0.648[b] |
| | 415.0[c] | 564.6[c] | 22.1[c] | 0.601[c] |
| | 466.5[d] | 633.7[d] | 22.8[d] | 0.630[d] |
| OFPMA[f] | 444.1[b] | 590.0[b] | 18.5[b] | 0.664[b] |
| | 437.8[c] | 589.8[c] | 20.3[c] | 0.619[c] |
| | 482.9[d] | 650.2[d] | 19.8[d] | 0.609[d] |

[a] Reference 9. [b] Estimated with the Joback method and Ambrose−Walton method. [c] Estimated with the modified Joback method and Ambrose−Walton method. [d] Estimated with the Constantinou−Gani method and Ambrose−Walton method. [e] 2,2,3,3,4,4,5,5-Octafluoropentyl acrylate. [f] 2,2,3,3,4,4,5,5-Octafluoropentyl methacrylate.

and Conatantinou−Gani method (black solid line) at 353.2 K. The values of adjustable parameters of the Peng−Robinson EOS for the carbon dioxide + OFPA (above) system at 353.2 K are $k_{ij}$ = 0.100 and $\eta_{ij}$ = 0.042 for the Joback method (red dashed line) (rmsd = 6.11 %, data point no. = 8), $k_{ij}$ = 0.093 and $\eta_{ij}$ = 0.045 for the modified Joback method (blue dashed line) (rmsd = 6.30 %, data point no. = 8), and $k_{ij}$ = 0.008 and $\eta_{ij}$ = −0.023 for the Constantinou−Gani method (black solid line) (rmsd = 3.65 %, data point no. = 8), respectively. The values of adjustable parameters of the Peng−Robinson EOS for the carbon dioxide + OFPMA (bottom) system at 353.2 K are $k_{ij}$ = 0.087 and $\eta_{ij}$ = 0.040 for the Joback method (red long dashed line) (rmsd = 6.03 %, data point no. = 8), $k_{ij}$ = 0.075 and $\eta_{ij}$ = 0.037 for the modified Joback method (blue short dashed line) (rmsd = 5.97 %, data point no. = 8), and $k_{ij}$ = 0.040 and $\eta_{ij}$ = 0.013 for the Constantinou−Gani method (black solid line) (rmsd = 4.03 %, data point no. = 8), respectively.

Figure 3 represents the comparison of the experimental data for the carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems with calculations obtained from the Peng−Robinson EOS using the Joback method, modified Joback method, and Constantinou−Gani method. Also, in Table 5 the calculation results obtained from the Peng−Robinson EOS using three methods are shown. As shown in Figure 3, we compared the experimental data with calculated values for the entire temperature range by using optimum parameters determined at 353.2 K. In the case of the Joback method, the critical constants by the Joback group contribution method were calculated for a simple fluorine segment (−F). Figure 3 plots the pressure against mole fraction to illustrate the comparison of the experimental data for the carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems with calculations (long dashed line) obtained with the Peng−Robinson EOS $k_{ij}$ equal to 0.100 and $\eta_{ij}$ equal to 0.042 in the case of carbon dioxide + OFPA system (above) (rmsd = 8.13 %, data point no. = 40), and $k_{ij}$ equal to 0.087 and $\eta_{ij}$ equal to 0.040 in the case of carbon dioxide + OFPMA system (bottom) (rmsd = 7.62 %, data point no. = 40) using the Joback method. As shown in Figure 3, the vapor−liquid equilibrium by the modified Joback method plots the pressure against mole fraction to illustrate the comparison of the experimental data for the carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems with calculations (short dashed line) obtained from the Peng−Robinson EOS $k_{ij}$ equal to 0.093 and $\eta_{ij}$ equal to 0.045 in the case of (carbon dioxide + OFPA) (above) (rmsd = 8.74 %, data point no. = 40), and $k_{ij}$ equal to 0.075 and $\eta_{ij}$ equal to 0.037 in the case of (carbon dioxide + OFPMA) (bottom) (rmsd = 7.62 %, data point no. = 40). The boiling point by the modified Joback method was calculated by using the fluorine segment and perfluorinated carbon (−F and $-CF_2-$). The boiling point calculated by group parameters (Table 3) is shown in Table 4.

Also, in the case of the Constantinou−Gani method, Figure 3 shows the comparison of the experimental data for the carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems with the calculations (solid line) obtained from the Peng−Robinson EOS, $k_{ij}$ equal to 0.008 and $\eta_{ij}$ equal to −0.023 for the (carbon dioxide + OFPA) system (above) (rmsd = 9.53 %, data point no. = 40) and $k_{ij}$ equal to 0.040 and $\eta_{ij}$ equal to 0.013 for the (carbon dioxide + OFPMA) system (bottom) (rmsd = 8.92 %, data point no. = 40) with a critical constant using the

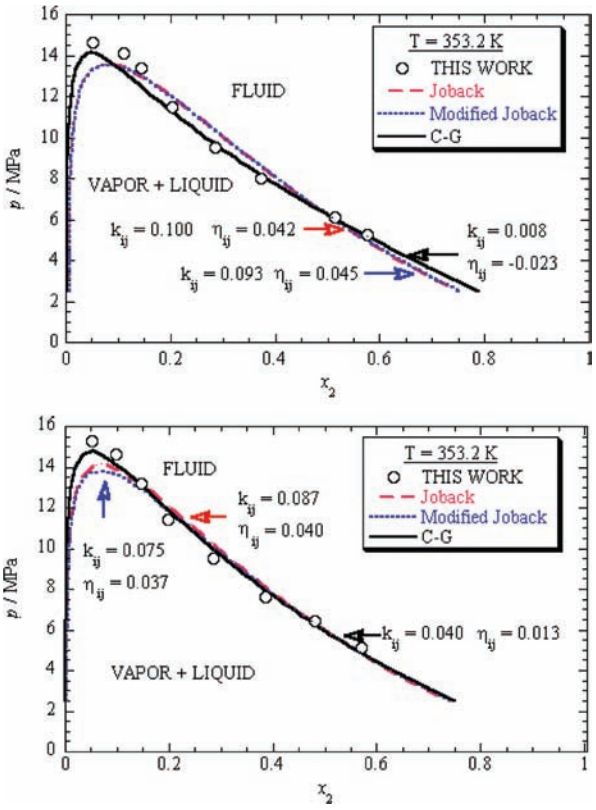

**Figure 5.** Comparison of experimental data (symbol) with the calculation result for the carbon dioxide (1) + OFPA (2) (above) and carbon dioxide (1) + OFPMA (2) (bottom) systems among the Joback method (red long dashed line), modified Joback method (blue short dashed line), and Conatantinou−Gani (C-G) method (black solid line) at 353.2 K.

Table 5. Result of rmsd and Optimized Parameters ($k_{ij}$ and $\eta_{ij}$) Determined by the Peng−Robinson EOS

| system | $T$/K | $k_{ij}$ | $\eta_{ij}$ | rmsd (%) | remarks |
|---|---|---|---|---|---|
| $CO_2$ + OFPA[a] | 313.2 K to 393.2 K | 0.100 | 0.042 | 8.13 | Joback method[c] |
| | | 0.093 | 0.045 | 8.74 | modified Joback method[d] |
| | | 0.008 | −0.023 | 9.53 | C-G method[e] |
| $CO_2$ + OFPMA[b] | 313.2 K to 393.2 K | 0.087 | 0.040 | 7.62 | Joback method[c] |
| | | 0.075 | 0.037 | 8.08 | modified Joback method[d] |
| | | 0.040 | 0.013 | 8.92 | C-G method[e] |

[a] 2,2,3,3,4,4,5,5-Octafluoropentyl acrylate. [b] 2,2,3,3,4,4,5,5-Octafluoropentyl methacrylate. [c] Joback group contribution method and Ambrose−Walton method. [d] Modified Joback group contribution method and Ambrose−Walton method. [e] Constantinou−Gani group contribution method and Ambrose−Walton method.

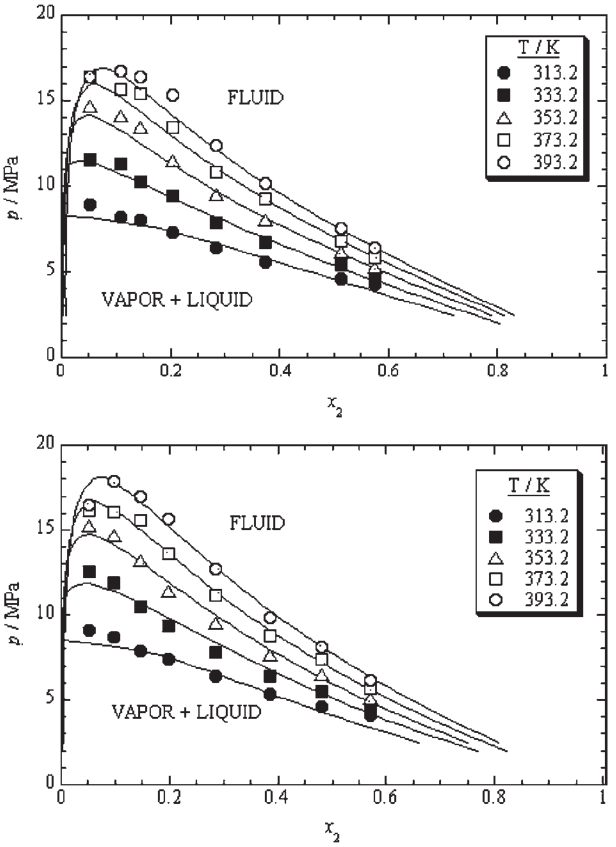

Figure 6. Plot of pressure against mole fraction that compares the experimental data (symbols) of the carbon dioxide (1) + OFPA (2) (above) and carbon dioxide (1) + OFPMA (2) (bottom) systems with calculations (solid lines) obtained with the Peng−Robinson EOS using optimum parameters ($k_{ij}$ and $\eta_{ij}$) at each temperature by Constantinou−Gani method. ●, 313.2 K; ■, 333.2 K; △, 353.2 K; □, 373.2 K; ○, 393.2 K.

Constantinou−Gani method. When we use the Constantinou−Gani method parameter, the calculation results show poor agreement with the experimental data for the (carbon dioxide + OFPA) and (carbon dioxide + OFPMA) systems. Nevertheless, the calculation was performed using optimized values determined at each temperature with critical properties from the Constantinou−Gani method. Calculation results are shown in Figure 6. As shown in Figure 6, the results show good agreement between experimental data (symbols) of the carbon dioxide + OFPA (above) (rmsd = 4.04 %, data point no. = 40) and carbon dioxide + OFPMA (bottom) (rmsd = 4.99 %, data point no. = 40) systems and calculated values (solid lines) obtained by the Peng−Robinson EOS using optimum parameters ($k_{ij}$ and $\eta_{ij}$) obtained at each temperature.

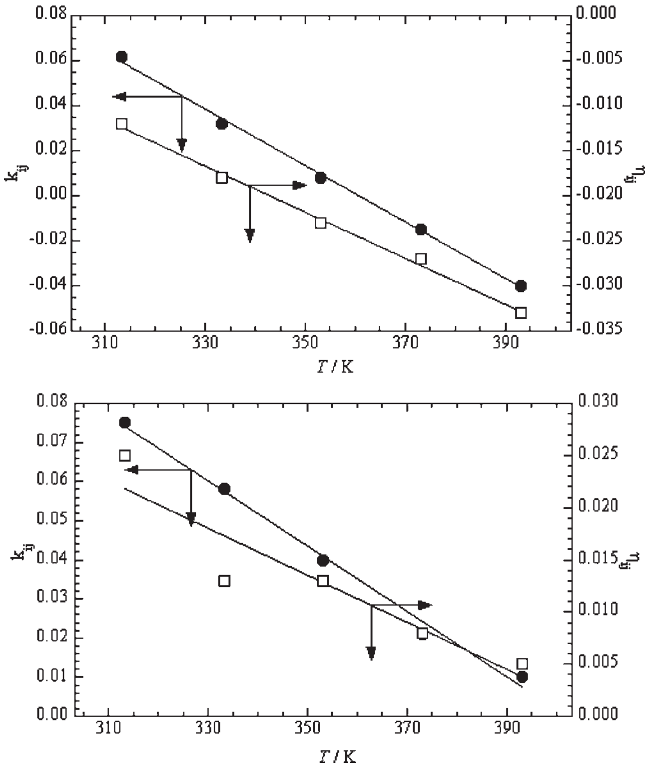

Figure 7. Plot of $k_{ij}$ and $\eta_{ij}$ parameters against temperature for the carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems with the Peng−Robinson EOS. The equations of the fitting line are $k_{ij} = -0.00125T + 0.45267$ and $\eta_{ij} = -0.000255T + 0.067466$ (313.2 K ≤ $T$ ≤ 393.2 K) in the case of carbon dioxide + OFPA and $k_{ij} = -0.000835T + 0.33572$ and $\eta_{ij} = -0.000225T + 0.09227$ (313.2 K ≤ $T$ ≤ 393.2 K) in the case of carbon dioxide + OFPMA systems.

Figure 7 plots the $k_{ij}$ and $\eta_{ij}$ parameters against temperature for the carbon dioxide + OFPA (above) and carbon dioxide + OFPMA (bottom) systems with the Peng−Robinson EOS. The equations of the fitting line are $k_{ij} = -0.0012T + 0.45267$ and $\eta_{ij} = -0.00025T + 0.06746$ (313.2 K ≤ $T$ ≤ 393.2 K) in the case of carbon dioxide + OFPA and $k_{ij} = -0.00083T + 0.33572$ and $\eta_{ij} = -0.00022T + 0.09227$ (313.2 K ≤ $T$ ≤ 393.2 K) in the case of carbon dioxide + OFPMA systems.

## 4. CONCLUSION

We measured pressure−composition ($P-x$) isotherms for binary mixtures of carbon dioxide + OFPA and carbon dioxide + OFPMA systems at temperatures from (313.2 to 393.2) K and pressures up to 17.86 MPa. A good correlation was obtained with the Peng−Robinson EOS with two adjustable binary interaction parameters.

When we use the Joback method, modified Joback method, and the Constantinou−Gani method to calculate critical constants, correlation results show a considerable underestimation or overestimation of pressure near the critical region. However, when we use the Joback and modified Joback method parameters for $-F$ and $-CF_2-$, correlation results show a slight underestimation of pressure near the critical region. The Joback and modified Joback method slightly underestimate the critical point, and the Constantinou−Gani method slightly overestimates it above 353.2 K and underestimates the critical point below 353.2 K.

A good agreement is shown in the comparison between the experimental data and the calculated value obtained at each temperature from the Peng−Robinson EOS for the carbon dioxide + OFPA and carbon dioxide + OFPMA systems. The rmsd's at five temperatures by the Constantinou−Gani method for the two systems range from (3.30 % to 5.62 %) for the (carbon dioxide + OFPA) and from (2.29 % to 7.76 %) for the (carbon dioxide + OFPMA) systems.

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## ■ REFERENCES

(1) Scheirs, J. *Modern Fluoropolymers*; John Wiley & Sons: New York, 1997.

(2) Byun, H. S.; Jang, Y. S.; Yoo, K. P. Phase behaviour for the carbon dioxide + 2-phenoxyethyl acrylate and carbon dioxide + 2-phenoxyethyl methacrylate systems at temperatures from (313.2 to 393.2) K and pressures from (5 to 31) MPa. *J. Chem. Thermodyn.* **2010**, *42*, 758–763.

(3) Liu, S.; Lee, H. Y.; Yoon, S. D.; Yoo, K. P.; Byun, H. S. High pressure phase behavior for poly[dodecyl methacrylate] + supercritical solvents + cosolvents and carbon dioxide + dodecyl methacrylate mixture. *Ind. Eng. Chem. Res.* **2009**, *48*, 7821–7827.

(4) Desimone, J. M.; Guan, Z.; Elsbernd, C. S. Synthesis of fluoropolymers in supercritical carbon dioxide. *Science* **1992**, *257*, 945–947.

(5) Darr, J. A.; Poliakoff, M. New directions in inorganic and metal-organic coordination chemistry in supercritical fluids. *Chem. Rev.* **1999**, *99*, 495–542.

(6) Kirby, C. F.; McHugh, M. A. Phase behavior of polymers in supercritical fluid solvents. *Chem. Rev.* **1999**, *99*, 565–602.

(7) Peng, D. Y.; Robinson, D. B. New two-constant equation of state. *Ind. Eng. Chem. Res. Fundam.* **1976**, *15*, 59–63.

(8) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth−Heinemann: Boston, 1994.

(9) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Liquids and Gases*, 5th ed.; McGraw-Hill: New York, 2001.

(10) Constantinou, L.; Gani, R. New group contribution method for estimating properties of pure compounds. *AIChE J.* **1994**, *40*, 1697–1710.

(11) Kim, S. H.; Park, M. H.; Lim, J. S.; Byun, H. S. High pressure phase behavior for the propionitrile and butyronitrile in supercritical carbon dioxide. *J. Ind. Eng. Chem.* **2010**, *16*, 962–966.

(12) Scott, R. L.; van Konynenburg, P. B. Static properties of solutions: van der Waals and related models for hydrocarbon system. *Discuss. Faraday Soc.* **1970**, *49*, 87–97.

(13) Kuester, J. L.; Mize, J. H. *Optimization techniques with Fortran*; McGraw−Hill Book Company: New York, 1973.

(14) Devotta, S.; Pendyala, V. R. Modified Joback group contribution method for normal boiling point of aliphatic halogenated compounds. *Ind. Eng. Chem. Res.* **1992**, *31*, 2042–2046.

(15) Bae, W.; Shin, H.; Kim, H. High pressure phase behavior of carbon dioxide + heptadecafluorodecyl acrylate and carbon dioxide + heptadecafluorodecyl methacrylate systems. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2295–2300.