

Experimental measurement and correlation of phase behavior for the CO₂+heptafluorobutyl acrylate and CO₂+heptafluorobutyl methacrylate systems at high pressure

Soon-Do Yoon and Hun-Soo Byun[†]

Department of Chemical and Biomolecular Engineering, Chonnam National University, Yeosu, Jeonnam 550-749, Korea
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Abstract—Experimental data of high pressure phase behavior from 313.2 to 393.2 K and pressures up to about 14.3 MPa were reported for binary mixture of 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) and 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) in supercritical carbon dioxide. The high pressure experiment was performed by static method using variable-volume view cell apparatus. The CO₂+HFBA and CO₂+HFBMA systems are correlated with the Peng-Robinson equation of state using a van der Waals one-fluid mixing rule. The CO₂+HFBA and CO₂+HFBMA systems exhibit type-I phase behavior with continuous critical mixture curves.

Keywords: Carbon Dioxide, 2,2,3,3,4,4,4-Heptafluorobutyl Acrylate, 2,2,3,3,4,4,4-Heptafluorobutyl Methacrylate, High Pressure Phase Behavior, Peng-Robinson EOS

INTRODUCTION

Thermodynamic knowledge on high-pressure phase behavior for the fluoro (meth) acrylate monomer containing supercritical carbon dioxide is required for practical uses. Fluoro (meth) acrylate monomers are used in a variety of coating applications because of their heat and chemical resistance, weatherability, low refractive index, non-cohesiveness, water and oil repellency, and electric insulating properties [1,2].

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 [3,4]. Supercritical carbon dioxide is a good solvent for low molecular weight and nonpolar molecules. Carbon dioxide has a quadrupole moment, no dipole moment, and low dielectric constant. Supercritical carbon dioxide used in this work is widely used as an environmentally benign solvent that is inexpensive, nonflammable, and nontoxic.

DeSimone et al. reported the first successful homogeneous free radical polymerization of fluoropolymers in supercritical carbon dioxide [5]. The phase behavior for a binary mixture of the fluoro (meth) acrylate with supercritical carbon dioxide plays an important role in fluoropolymer processes with a polymerization optimum condition and in various industrial applications [6].

Recently, phase behavior data for the CO₂+fluoric monomer systems were reported by Jang et al. [7] and Bae et al. [8]. Jang et al. used a static-type variable-volume view cell to measure the phase equilibria curves for the CO₂+octafluoropentyl acrylate and CO₂+octafluoropentyl methacrylate systems at temperatures ranging from 313.2 K to 393.2 K and pressure up to 17.86 MPa. Bae et al. reported high-pressure experimental data for the CO₂+heptadecafluorodecyl

acrylate and CO₂+heptadecafluorodecyl methacrylate systems at temperatures ranging from 323 K to 353 K and pressure up to 14.0 MPa. Therefore, it is very important to have a thermodynamic understanding on measuring and calculating phase behavior for the CO₂+fluoric monomer system.

In this work, the measurement is aimed at obtaining the phase equilibrium data for CO₂+HFBA and CO₂+HFBMA mixtures by investigating mixtures of carbon dioxide with two component using a variable volume view cell at temperatures ranging from (313.2 K to 393.2 K) and pressure up to 14.3 MPa. Also, the pressure-composition (p-x) diagrams of the mixture critical curve are presented for the CO₂+HFBA and CO₂+HFBMA systems at the five temperatures. The experimental data for CO₂+HFBA and CO₂+HFBMA systems obtained in this work are correlated with the Peng-Robinson equation of state [9,10] using the van der Waals one-fluid mixing rules including two adjustable parameters. The properties of critical pressure, critical temperature and acentric factor of HFBA and HFBMA are reported in the data calculated by Joback and Lydersen group contribution method [11], while the vapor pressure is estimated by the Lee-Kesler method [11].

EXPERIMENTAL SECTION

1. Materials

Carbon dioxide (CO₂, CAS RN 124-38-9, purity >99.99%) was obtained from Deokyang Co (Korea) and used as received. 2,2,3,3,4,4,4-Heptafluorobutyl acrylate (H₂C=CHCO₂CH₂CF₂CF₂CF₃, CAS RN 424-64-6, purity: 97%) and 2,2,3,3,4,4,4-heptafluorobutyl methacrylate (H₂C=C(CH₃)CO₂CH₂CF₂CF₂CF₃, CAS RN 13695-31-3, purity: 97%) used in this work were obtained from Alfa Aesar Co. Both components were used without further purification in the experiments.

2. Apparatus and Procedure

To obtain high-pressure phase behavior data, a high pressure ex-

[†]To whom correspondence should be addressed.

E-mail: hsbyun@jnu.ac.kr

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perimental apparatus (variable-volume view cell in static-type) was used. This experimental apparatus has already been described in detail elsewhere. [12] The main components of the experimental system are variable volume view cell, high-pressure generator and visual apparatus. The variable volume view cell is capable of operating up to pressure of 70 MPa. The inside of the view cell was purged several times with nitrogen and carbon dioxide to remove traces of air and organic matter. The measured amount of monomer is loaded into the cell to within ± 0.0005 g using a syringe. Carbon dioxide was added to the cell to within ± 0.002 g using a high pressure bomb. The piston (2.54 cm length) in the view cell was moved using water pressurized by a high pressure generator (HIP, model 37-5.75-60). The pressure of mixture is measured with a Heise gauge (Dresser Ind., model CM-53920, (0 to 34.0) MPa) accurate to within ± 0.02 MPa. The temperature in the cell was maintained to within ± 0.2 K and measured to within ± 0.2 K. The visual status of the inside of the cell 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 F100-038-000-50) set toward the sapphire window.

The mixture in the view cell is compressed to a single-phase (fluid) at high-pressure and at high-temperature, and it is maintained in the single-phase region at the desired temperature for at least 30-

40 min for the cell to reach phase equilibrium. The pressure is then slowly decreased until a second phase appears. A bubble point pressure is obtained when small vapor bubbles appear first in the cell, while a dew point is obtained if a fine mist appears in the cell. The vicinity region of mixture-critical point is sensitive to a slight change in either pressure or temperature. A slight change in pressure (or temperature) for the mixture-critical point causes a dramatic change in the amount of one phase or two phases present in the cell [12].

Table 1. Experimental data for the CO₂ (1-x)+2,2,3,3,4,4,4-heptafluorobutyl acrylate {H₂C=C(CH₃)CO₂CH₂CF₂CF₂CF₃} (x) system. BP is a bubble point, CP is a critical point and DP is a dew point

x	p/MPa	Transition
T/K=313.2		
0.051	8.71	BP
0.096	8.10	BP
0.147	7.41	BP
0.206	6.66	BP
0.290	5.72	BP
0.405	4.54	BP
0.478	3.84	BP
T/K=333.2		
0.051	11.29	BP
0.096	10.59	BP
0.147	9.48	BP
0.206	8.31	BP
0.290	7.00	BP
0.405	5.50	BP
0.478	4.70	BP
T/K=353.2		
0.051	13.28	BP
0.096	12.66	BP
0.147	11.61	BP
0.206	10.14	BP
0.290	8.52	BP
0.405	6.59	BP
0.478	5.69	BP
T/K=373.2		
0.051	12.10	DP
0.096	13.79	CP
0.147	13.15	BP
0.206	12.00	BP
0.290	9.83	BP
0.405	7.62	BP
0.478	6.38	BP
T/K=393.2		
0.051	12.97	DP
0.096	14.19	DP
0.147	14.31	CP
0.206	13.10	BP
0.290	11.15	BP
0.405	8.55	BP
0.478	7.10	BP

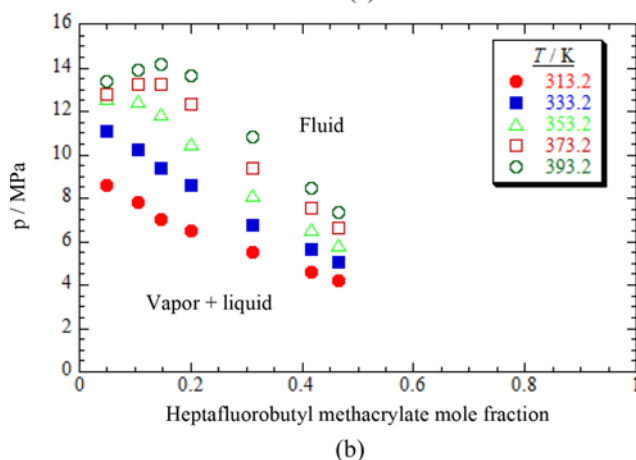
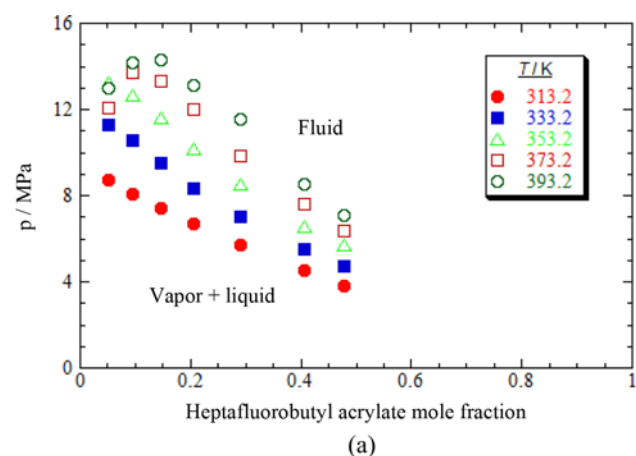


Fig. 1. Pressure-composition isotherms for the carbon dioxide+2,2,3,3,4,4,4-heptafluorobutyl acrylate (a) and carbon dioxide+2,2,3,3,4,4,4-heptafluorobutyl methacrylate (b) systems obtained in this work.

RESULTS AND DISCUSSION

High pressure experimental data for the CO₂+HFBA and CO₂+HFBMA systems were measured, and the experimental uncertainty was estimated to ± 0.02 MPa and ± 0.2 K for a given loading of the cell. The combined standard uncertainties of HFBA and HFBMA mole fractions were estimated to be ± 0.0008 [13].

Fig. 1(a) and 1(b), Table 1 and Table 2 show pressure-composi-

Table 2. Experimental data for the CO₂ (1-x)+2,2,3,3,4,4,4-heptafluorobutyl methacrylate {H₂C=C(CH₃)CO₂CH₂CF₂CF₃} (x) system. BP is a bubble point, CP is a critical point and DP is a dew point

x	p/MPa	Transition
T/K=313.2		
0.049	8.59	BP
0.105	7.78	BP
0.146	7.05	BP
0.201	6.48	BP
0.310	5.51	BP
0.416	4.57	BP
0.465	4.17	BP
T/K=333.2		
0.049	11.07	BP
0.105	10.27	BP
0.146	9.41	BP
0.201	8.59	BP
0.310	6.76	BP
0.416	5.62	BP
0.465	5.03	BP
T/K=353.2		
0.049	12.59	DP
0.105	12.48	CP
0.146	11.90	BP
0.201	10.52	BP
0.310	8.16	BP
0.416	6.53	BP
0.465	5.86	BP
T/K=373.2		
0.049	12.79	DP
0.105	13.28	DP
0.146	13.28	BP
0.201	12.31	BP
0.310	9.41	BP
0.416	7.52	BP
0.465	6.66	BP
T/K=393.2		
0.049	13.41	DP
0.105	13.90	DP
0.146	14.14	CP
0.201	13.62	BP
0.310	10.79	BP
0.416	8.48	BP
0.465	7.35	BP

tion (p-x) isotherms for the CO₂+HFBA and CO₂+HFBMA systems at T=313.2, 333.2, 353.2, 373.2 and 393.2 K and pressure up to 14.3 MPa. The CO₂+HFBA and CO₂+HFBMA systems do not exhibit three phases at the five temperatures investigated. The experimental data for the CO₂+HFBA and CO₂+HFBMA systems have not been found in the literature. The P-x isotherms shown in Fig. 1 are consistent with those expected for a type-I system where a maximum occurs in the critical mixture curve [14,15]. The solubility of CO₂ in the liquid phase decreases as the temperatures shift higher under constant pressure.

In this work, the experimental phase behavior data are correlated with the PR-EOS [9] using van der Waals one fluid mixing rules. PR-EOS is expressed as follows:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (1)$$

$$a(T) = 0.457235 \frac{R^2 T_c^2}{p_c} \alpha(T) \quad (2)$$

$$b(T_c) = 0.077796 \frac{RT_c}{p_c} \quad (3)$$

$$\alpha(T) = [1 + K(1 - T_r^{0.5})]^2 \quad (4)$$

$$K = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

where, p_c and T_c are the critical pressure and temperature of pure components, and ω is the acentric factor. The van der Waals one-fluid mixed rules are expressed as follows:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

$$a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (7)$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \quad (8)$$

$$b_{ij} = \frac{b_{ii} + b_{jj}}{2} (1 - \eta_{ij}) \quad (9)$$

where k_{ij} and η_{ij} are binary interaction parameters determined by regression experimental data from the PR-EOS. Objective function (OBF) [16] and root mean squared relative deviation (RMSD) percent of this calculation were defined as follows:

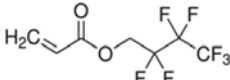
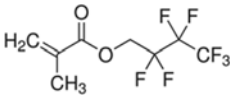
$$OBF = \sum_i^N \left(\frac{P_{exp} - P_{cal}}{P_{exp}} \right)^2 \quad (10)$$

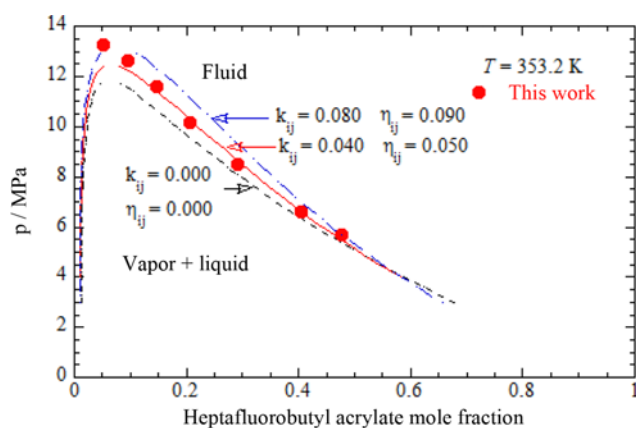
$$RMSD(\%) = \sqrt{\frac{OBF}{ND}} \times 100 \quad (11)$$

ND in Eq. (11) means the number of data points. Table 3 lists the pure component critical temperature (T_c), critical pressure (P_c) and acentric factor (ω) for carbon dioxide [11], HFBA [11] and HFBMA [11] that are used with the PR-EOS. The boiling points of HFBA [17] and HFBMA [18] were obtained from the literature. The critical temperature, critical pressure and acentric factor (ω) of HFBA and HFBMA were estimated by Joback-Lydersen method [11].

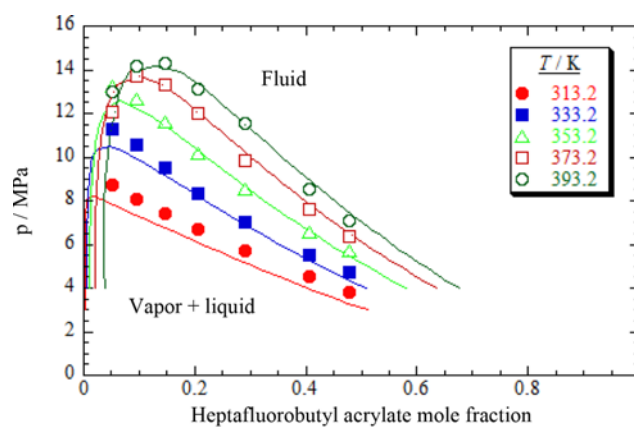
Fig. 2(a) and 2(b) represent the comparison between experimental data and calculated values obtained using PR-EOS for CO₂+

Table 3. Pure component critical properties used for the Peng-Robinson equation state

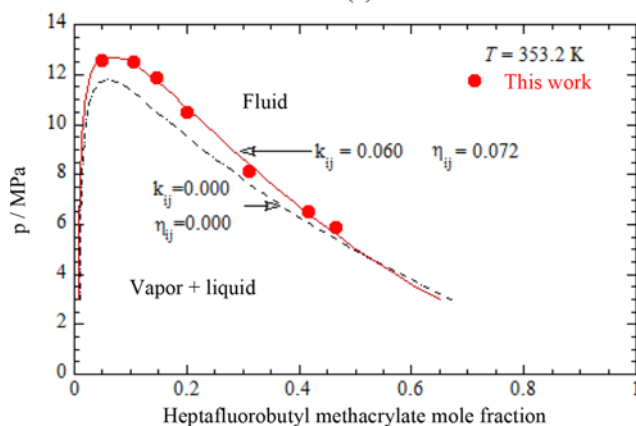
Component	M _w	Chemical structure	T _b /K	T _c /K	p _c /MPa	ω
Carbon dioxide	44.01	O=C=O		304.2	7.37	0.225
2,2,3,3,4,4,4-Heptafluorobutyl acrylate	254.10		397.7 ^a	544.3	2.27	0.569
2,2,3,3,4,4,4-Heptafluorobutyl methacrylate	268.13		408.1 ^b	552.9	2.08	0.585

^acas.ChemNet.com^bSigma-Aldrich

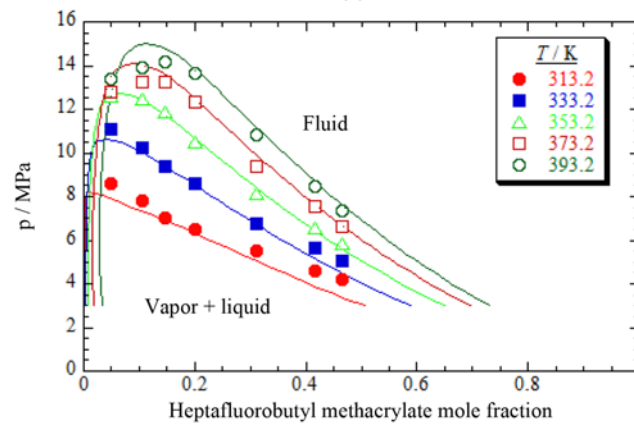
(a)



(a)



(b)



(b)

Fig. 2. Comparison of the best fit of Peng-Robinson equation of state to CO₂+2,2,3,3,4,4,4-heptafluorobutyl acrylate (a) and CO₂+2,2,3,3,4,4,4-heptafluorobutyl methacrylate (b) systems obtained in this work (●) at 353.2 K.

HFBA (a) and CO₂+HFBMA (b) systems at 353.2 K. The binary interaction parameters of PR-EOS are fitted by the experimental data at 353.2 K. The values of optimized parameters of PR-EOS for the CO₂+HFBA (a) and CO₂+HFBMA (b) systems are $k_{ij}=0.040$ and $\eta_{ij}=0.050$ (RMSD=3.33%, data point no.=7), and $k_{ij}=0.060$ and $\eta_{ij}=0.072$ (RMSD=2.31%, data point no.=7), respectively. Especially, the value of optimized parameters for the CO₂+HFBA (a) system was compared against $k_{ij}=0.000$ and $\eta_{ij}=0.000$, $k_{ij}=0.040$ and $\eta_{ij}=0.050$, and $k_{ij}=0.080$ and $\eta_{ij}=0.090$ at 353.2 K. The results

Fig. 3. A comparison of the experimental data (symbols) for the CO₂+2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) (a) and CO₂+2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) (b) systems with calculations (solid lines) obtained using the Peng-Robinson equation of state with k_{ij} equal to 0.040 and η_{ij} equal to 0.050 (CO₂+HFBA) and k_{ij} equal to 0.060 and η_{ij} equal to 0.072 (CO₂+HFBMA).

of the comparisons show a good agreement except for one point ($x=0.051$) in case of $k_{ij}=0.040$ and $\eta_{ij}=0.050$, and a poor agreement except for two points ($x=0.051, 0.478$) in case of $k_{ij}=0.080$ and $\eta_{ij}=0.090$. Therefore, we adopted a lower error in case of $k_{ij}=0.040$ and $\eta_{ij}=0.050$ as an optimum parameter.

Fig. 3(a) shows the comparison between experimental data and

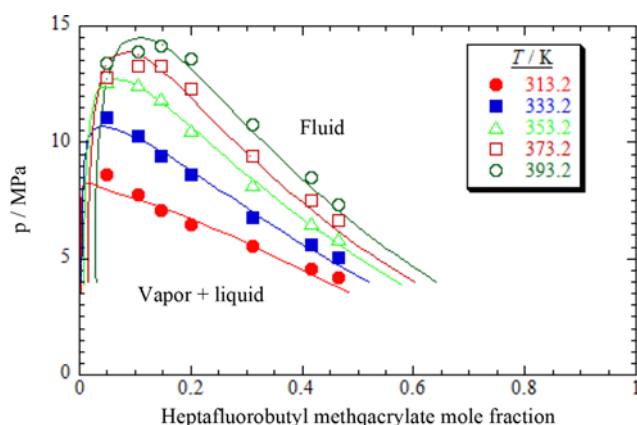
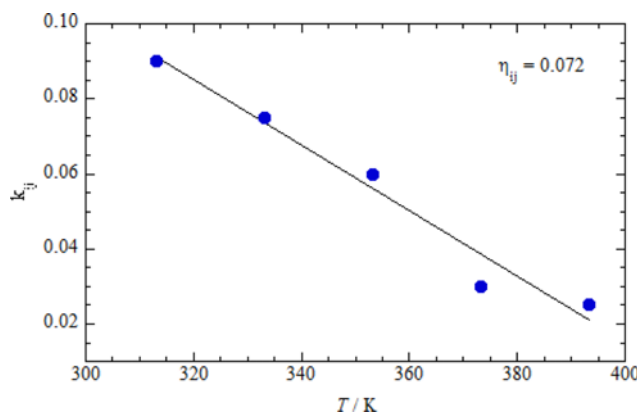
Table 4. Data of k_{ij} and η_{ij} parameters and the value of RMSD against temperature for the CO_2 +2,2,3,3,4,4,4-heptafluorobutyl methacrylate system with the Peng-Robinson equation of state

		313.2 K	333.2 K	353.2 K	373.2 K	393.2 K
2,2,3,3,4,4,4-Heptafluorobutyl methacrylate	k_{ij}	0.090	0.075	0.060	0.030	0.025
	η_{ij}	0.072	0.072	0.072	0.072	0.072
	RMSD	5.22%	3.75%	2.31%	3.67%	3.56%

calculated pressure-composition (P-x) isotherms at temperatures of (313.2, 333.2, 353.2, 373.2 and 393.2) K for the CO_2 +HFBA system using the optimized values of $k_{ij}=0.040$ and $\eta_{ij}=0.050$ (RMSD=3.33%, data point no.=7) determined at 353.2 K. As shown in Fig. 3(a), RMSD for the CO_2 +HFBA system was 5.11% and ND is 35 points at the five temperatures.

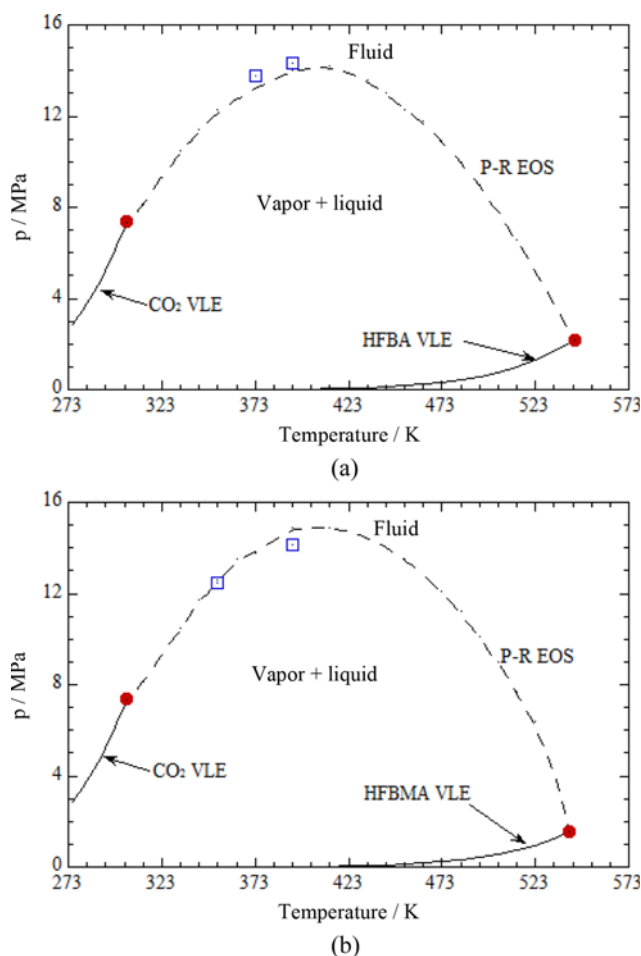
Fig. 3(b) compares the experimental results with calculated P-x isotherms at T=313.2, 333.2, 353.2, 373.2 and 393.2 K for the CO_2 +HFBMA system. These isotherms were calculated by using the optimized values of $k_{ij}=0.060$ and $\eta_{ij}=0.072$ (RMSD=2.31%, data point no.=7) determined at 353.2 K. The calculated curves by the PR-EOS were not observed for three phases at the five temperatures. RMSD for the CO_2 +HFBMA system was 5.30% and ND was 35 points at the five temperatures.

RMSD for the CO_2 +HFBMA system was quite high when the

**Fig. 4. Curves of the best fit for the CO_2 +2,2,3,3,4,4,4-heptafluorobutyl methacrylate system obtained at each temperature.****Fig. 5. Tendency curve of k_{ij} parameter according to temperature for the CO_2 +2,2,3,3,4,4,4-heptafluorobutyl methacrylate system.**

parameters were applied to these systems. So we needed to obtain optimized parameters for each temperature to reduce RMSD. The RMSD result is shown in Table 4.

Fig. 4 represents the pressures against mole fraction in order to compare the experimental data (symbols) of the CO_2 +HFBMA system with calculations (solid lines) obtained with the PR-EOS at each temperature. As shown, the calculated curves were performed using optimized values determined at each temperature. RMSD at five

**Fig. 6. Pressure-temperature diagram for the CO_2 +2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) (a) and CO_2 +2,2,3,3,4,4,4-heptafluorobutyl methacrylate (HFBMA) (b). The solid line and the solid circles represent the vapor-liquid line and the critical point for pure carbon dioxide and HFBA or HFBMA. The open squares are critical points determined from isotherms measured in this study. The dashed line represents calculated values obtained using the Peng-Robinson equation of state with k_{ij} equal to 0.040 and η_{ij} equal to 0.050 (a) and k_{ij} equal to 0.060 and η_{ij} equal to 0.072 (b).**

temperatures (313.2, 333.2, 353.2, 373.2 and 393.2) K for the CO₂+HFBMA system was 5.22%, 3.75%, 2.31%, 3.67% and 3.56%, respectively. Here, ND is 7 at each temperature. As a result of applying optimum parameters for each temperature to the CO₂+HFBMA system, the comparison between the experimental data and calculated curves presents a better agreement at each temperature than calculated values shown in Fig. 3(b).

Fig. 5 plots k_{ij} and η_{ij} parameters which were obtained from the PR-EOS against temperature for the CO₂+HFBMA system at each temperature. The equations of parameters for the fitting line were $k_{ij}=0.36505-8.75\times 10^{-4}T$ and $\eta_{ij}=0.072$ at temperature ranges from (313.2 K to 393.2 K) in the case of CO₂+HFBMA.

Fig. 6(a) and (b) compare the critical mixture curves of the experimental data with the values calculated by the Peng-Robinson equation of state for the CO₂+HFBA (a) and CO₂+HFBMA (b) systems. The calculated critical mixture curve showed type-I, in good agreement with experimental observations at two temperatures. In Fig. 6, solid lines represent the vapor pressure for pure CO₂ [11], HFBA [11] and HFBMA [11]. The solid lines represent the vapor pressures of pure HFBA and HFBMA, which were obtained by the Lee-Kesler method [11]. The solid circles represent the critical point for pure CO₂ and HFBA, and CO₂ and HFBMA. The upper part of the dashed line is in single phase (fluid), while the lower part is vapor-liquid (two-phases). The dashed lines represent the calculated values obtained by the Peng-Robinson equation of state, with $k_{ij}=0.040$ and $\eta_{ij}=0.050$ (for HFBA (a)) and $k_{ij}=0.060$ and $\eta_{ij}=0.072$ (for HFBMA (b)). The open squares represent the mixture critical points determined from isotherms measured in this experiment.

CONCLUSIONS

High pressure experimental data for CO₂+HFBA and CO₂+HFBMA binary mixture systems were measured using a static method comprised of a variable-volume view cell apparatus at temperature ranges from 313.2 K to 393.2 K and pressure up to 14.3 MPa. These two systems exhibit type-I phase behavior and do not exhibit three phase at any five temperatures. The Peng-Robinson equation of state is able to predict the phase behavior for the two systems using two binary mixture interaction parameters (k_{ij} and η_{ij}) obtained at 353.2 K. RMSD for the CO₂+HFBA and CO₂+HFBMA systems using two parameters determined at 353.2 K were 5.11% and 5.30%, respectively. When applying optimized parameters for each temperature for the CO₂+HFBMA system, RMSD for the CO₂+HFBMA system was within error range from 2.31% to 5.22%. As a result, it shows a good agreement between calculated curves and experimental data when the Peng-Robinson equation of state with two optimized

parameters at each temperature was used.

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