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High-Pressure Phase Behavior of Carbon Dioxide + Tetrahydrofurfuryl Acrylate and Carbon Dioxide + Tetrahydrofurfuryl Methacrylate Binary Mixture Systems

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ABSTRACT: In this study, the high-pressure phase behavior of carbon dioxide + tetrahydrofurfuryl acrylate and carbon dioxide + tetrahydrofurfuryl methacrylate mixtures was studied using a variable volume view cell at temperatures ranging from (313.15 to 363.15) K and pressures of up to 18 MPa. The experimental results were correlated with the Peng−Robinson equation of state using the van der Waals one-fluid mixing rule with one adjustable binary interaction parameter. We compared the Nannoolal−Rarey and Constantinou−Gani group contribution methods for the correlation of the experimental results.

INTRODUCTION

Poly(tetrahydrofurfuryl acrylate) (poly(THF-A)) is used as an intermediate in the manufacturing of plasticizers, coating materials, and printing materials.[1] Poly(tetrahydrofurfuryl methacrylate) (poly(THFMA)) has found use as a component in paint-on artificial finger nails and in low-shrinkage dental and biomedical materials.[2] Poly(THFMA) has also found useful applications in the formulation of copolymer loadable-latexes.[3]

The purities of THF-A and THFMA, which are monomers of poly(THF-A) and poly(THFMA), are generally improved by batch distillation. However, this process causes a certain amount of oligomers to be produced, due to the high operating temperature, which causes a low yield to be obtained. To overcome this problem, an economic and effective separation method is required. Supercritical fluid extraction (SFE) operates at a lower temperature and is more economic and efficient than the traditional method. Especially, supercritical carbon dioxide (scCO_2), which is used in SFE as a solvent, is easy to remove, simply by reducing the pressure and leaving almost no trace, and the CO_2 is almost always recovered.[4] Thermodynamic data, such as the bubble, dew, and critical points, are essential for the design of an SFE process for THF-A and THFMA, but experimental data for these binary systems are rare.

In this work, we measured the critical point, bubble point, and dew point pressures for the binary mixtures consisting CO_2 + THF-A and CO_2 + THFMA at temperatures ranging from (313.15 to 363.15) K and pressures of up to 18 MPa.

EXPERIMENTAL SECTION

1. Materials. Carbon dioxide (99.999 mol % minimum purity) was purchased from Korea Industrial Gases. THF-A (CAS No. 2399-48-6) and THFMA (CAS No. 2455-24-5) were obtained from Miwon Specialty Chemical Co., Ltd. They were used without further purification, and its purity was at least 98.5 mol % as determined by gas chromatographic (GC) analysis. Figure 1 shows the chemical structures of THF-A and THFMA.

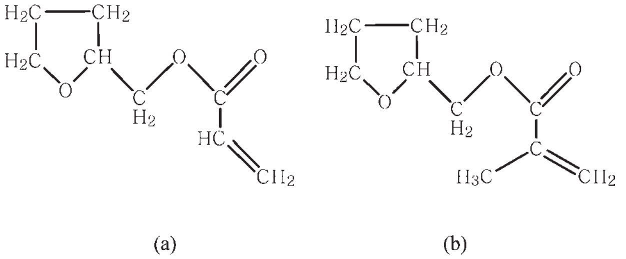

Figure 1. Chemical structure of (a) tetrahydrofurfuryl acrylate and (b) tetrahydrofurfuryl methacrylate.

2. Apparatus. The bubble, critical, and dew point data were obtained with a variable volume view cell apparatus, which is described in detail elsewhere.[5−7] Experiments of the CO_2 + THF-A and CO_2 + THFMA systems used the following procedures. A measured amount of the material was loaded into a cell with a syringe to within ± 0.001 g. Before the CO_2 was added to it, the cell was initially purged two or three times with an inert gas and CO_2 at room temperature to remove all traces of air and chemicals. Then, a predetermined amount of CO_2 was added to the cell to within ± 0.01 g using a high-pressure CO_2 bomb.

With the temperature of the cell kept fixed, the pressure was increased by a high-pressure generator (High Pressure Equipment Co., model 62-6-10) until the mixture formed a single phase. A magnetic stirring bar in the cell helped the mixture to reach equilibrium quickly. Once the solution formed a single phase, the pressure was slowly decreased until the bubble, dew, or mixture critical point was reached. This procedure was repeated until the variation of the phase transition pressure was minimized

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Table 1. Estimation Results with Critical Constants and Acentric Factors for the Peng−Robinson Equation of State

component	T_C/K	P_C/MPa	ω	remark
CO_2	304.1[a]	7.38[a]	0.225[a]	
THF-A	662.1	3.07	0.368	N-R[b]
	657.5	3.07	0.480	C-G[c]
THFMA	657.6	2.60	0.424	N-R[b]
	656.7	2.50	0.516	C-G[c]

[a] Reference 13. [b] Nannoolal−Rarey group contribution method and Lee−Kesler method. [c] Constantinou−Gani group contribution method and Lee−Kesler method.

Table 2. Experimental Data for the CO_2 + Tetrahydrofurfuryl Acrylate System

T/K	P/MPa	mole fraction of CO_2	transition[a]
363.15	10.03	0.570	BP
	10.55	0.604	BP
	11.62	0.646	BP
	13.14	0.689	BP
	13.91	0.741	BP
	15.55	0.788	BP
	16.84	0.846	BP
	17.29	0.889	BP
	17.17	0.908	DP
	16.85	0.934	DP
353.15	8.89	0.570	BP
	9.70	0.604	BP
	10.58	0.646	BP
	11.82	0.689	BP
	12.47	0.741	BP
	13.91	0.788	BP
	15.18	0.846	BP
	15.49	0.889	BP
	15.55	0.908	DP
	15.20	0.934	DP
343.15	7.94	0.570	BP
	8.55	0.604	BP
	9.22	0.646	BP
	10.41	0.689	BP
	10.85	0.741	BP
	12.15	0.788	BP
	13.23	0.846	BP
	13.64	0.889	BP
	13.74	0.908	DP
	13.41	0.934	DP
333.15	6.98	0.570	BP
	7.57	0.604	BP
	8.10	0.646	BP
	9.00	0.689	BP
	9.30	0.741	BP
	10.57	0.788	BP
	11.41	0.846	BP
	11.48	0.889	BP
	11.75	0.908	DP
	11.52	0.934	DP
323.15	6.15	0.570	BP
	6.34	0.604	BP
	6.94	0.646	BP
	7.75	0.689	BP
	8.07	0.741	BP
	8.94	0.788	BP
	9.71	0.846	BP
	9.63	0.889	BP
	9.77	0.908	BP
	9.70	0.934	BP
313.15	5.19	0.570	BP
	5.64	0.604	BP
	5.95	0.646	BP
	6.56	0.689	BP
	6.71	0.741	BP
	7.30	0.788	BP
	8.26	0.846	BP
	8.05	0.889	BP
	7.97	0.908	BP
	7.93	0.934	BP

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

to within ± 0.4 MPa, and the average pressure, which is the average of the last three measured pressures, was recorded as the experimental result. The pressure of the solution was determined by measuring the water pressure with a digital pressure transducer (Paroscientific Inc., model 43KR-HHT-101, accuracy of 0.01 %) and indicator (Paroscientific, Inc., model no. 730). The temperature was measured with a PRT type thermometer (HART Scientific, Inc., model 5622-32SR, accuracy of ± 0.045 K) and a thermometer fixed to the surface of the cell and displayed by an indicator (Hart Scientific, Inc., model 1502). The temperature of the cell was maintained to within ± 0.1 K and measured to within ± 0.1 K. The inside of the cell was shown on a monitor using a camera (Veltek International, Inc., model CVC5520) with a borescope (Olympus Corp., model R100-038-00-50) set toward the sapphire window.

The calibration of the pressure transducer and thermometer was done by the Korea Testing Laboratory (KTL), the national calibration laboratory. The uncertainty of the thermometer was 0.022 K, and that of the pressure transducer was 0.002 MPa.

■ THERMODYNAMIC MODEL

The experimental data obtained in this study were correlated with the Peng−Robinson equation of state (PR-EOS) using the van der Waals one-fluid mixing rule including one binary interaction parameter (k_{ij}).[8] The PR-EOS is defined as follows.

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

The mixture parameters used in PR-EOS are determined by the van der Waals one-fluid mixing rule.

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{2}$$

Table 3. Experimental Data for the CO_2 + Tetrahydrofurfuryl Methacrylate System

T/K	P/MPa	mole fraction of CO_2	transition[a]
363.15	10.10	0.565	BP
	10.66	0.609	BP
	11.61	0.651	BP
	12.56	0.684	BP
	13.60	0.725	BP
	14.65	0.766	BP
	15.30	0.785	BP
	16.44	0.828	BP
	16.64	0.85	BP
	17.24	0.887	BP
	17.41	0.9	DP
	17.52	0.921	DP
	17.70	0.938	DP
	17.20	0.946	DP
353.15	9.04	0.565	BP
	9.96	0.609	BP
	10.55	0.651	BP
	11.15	0.684	BP
	12.34	0.725	BP
	13.04	0.766	BP
	13.70	0.785	BP
	14.62	0.828	BP
	15.02	0.85	BP
	15.44	0.887	BP
	15.70	0.9	DP
	15.79	0.921	DP
	16.01	0.938	DP
	15.61	0.946	DP
343.15	8.00	0.565	BP
	8.73	0.609	BP
	9.23	0.651	BP
	9.85	0.684	BP
	10.86	0.725	BP
	11.36	0.766	BP
	12.08	0.785	BP
	12.76	0.828	BP
	13.26	0.85	BP
	13.50	0.887	BP
	13.80	0.9	DP
	13.90	0.921	DP
	14.16	0.938	DP
	13.80	0.946	DP
333.15	6.97	0.565	BP
	7.87	0.609	BP
	8.04	0.651	BP
	8.50	0.684	BP
	9.39	0.725	BP
	9.66	0.766	BP
	10.43	0.785	BP
	10.86	0.828	BP
	11.39	0.85	BP
	11.44	0.887	BP
	11.71	0.9	DP
	11.86	0.921	DP
	12.20	0.938	DP
	11.82	0.946	DP
323.15	6.18	0.565	BP
	6.87	0.609	BP
	7.09	0.651	BP
	7.28	0.684	BP
	8.10	0.725	BP
	8.20	0.766	BP
	8.87	0.785	BP
	9.04	0.828	BP
	9.40	0.85	BP
	9.44	0.887	BP
	9.69	0.9	BP
	9.82	0.921	BP
	10.15	0.938	BP
	9.88	0.946	BP
313.15	5.28	0.565	BP
	6.03	0.609	BP
	6.02	0.651	BP
	6.04	0.684	BP
	6.68	0.725	BP
	6.86	0.766	BP
	7.45	0.785	BP
	7.47	0.828	BP
	7.53	0.85	BP
	7.70	0.887	BP
	7.87	0.9	BP
	8.05	0.921	BP
	8.31	0.938	BP
	8.06	0.946	BP

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

Table 4. Calculation Results with the Peng−Robinson Equation of State

T/K	k_{ij}	AADP (%)	remark
	CO_2 + Tetrahydrofurfuryl Acrylate System		
313.15−363.15	0.0601	2.31	N-R[a]
	0.0444	1.91	C-G[b]
	CO_2 + Tetrahydrofurfuryl Methacrylate System		
313.15−363.15	0.0745	3.25	N-R[a]
	0.0645	2.59	C-G[b]

[a] Nannoolal−Rarey method and Lee−Kesler method. [b] Constantinou−Gani method and Lee−Kesler method.

$$b = \sum_i x_i b_i \qquad (3)$$

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \qquad (4)$$

The binary interaction parameter k_{ij} used in the one-fluid mixing rule is determined by the regression of the experimental data with the simplex method algorithm.

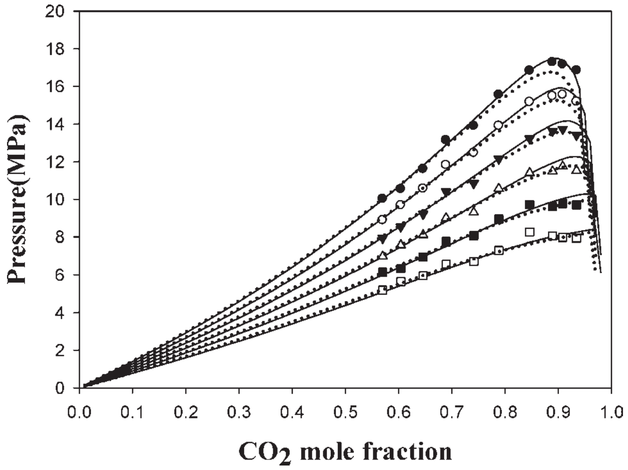

Figure 2. Calculation result using the group contribution method (T_C, P_C) and Lee–Kesler method (ω) for the CO_2 + tetrahydrofurfuryl acrylate system. ●, 363.15 K; ○, 353.15 K; ▼, 343.15 K; △, 333.15 K; ■, 323.15 K; □, 313.15 K. Solid lines, Constantinou–Gani method; dotted lines, Nannoolal–Rarey method.

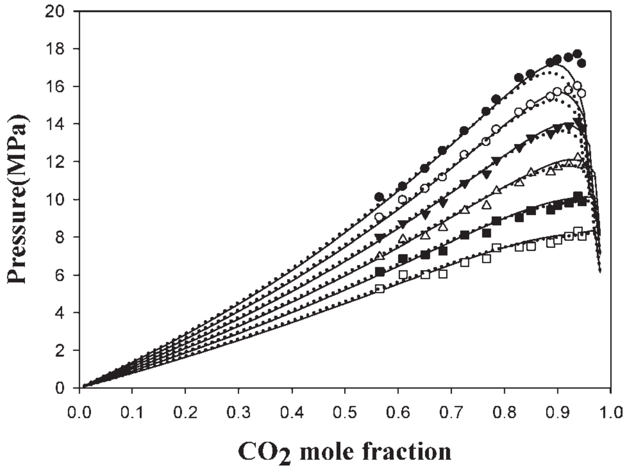

Figure 3. Calculation result using the group contribution method (T_C, P_C) and Lee–Kesler method (ω) for the CO_2 + tetrahydrofurfuryl methacrylate system. ●, 363.15 K; ○, 353.15 K; ▼, 343.15 K; △, 333.15 K; ■, 323.15 K; □, 313.15 K. Solid lines, Constantinou–Gani method; dotted lines, Nannoolal–Rarey method.

The critical temperature (T_C), pressure (P_C), and acentric factor (ω) of THF-A and THFMA are necessary to correlate the experimental results with PR-EOS. However, there are no experimental results available for the critical properties of these materials. Therefore, the critical constants and acentric factor were estimated using the group contribution and Lee–Kesler methods,[9] respectively. In this work, the critical constants were estimated using the Nannoolal–Rarey group contribution method[10,11] and Constantinou–Gani group contribution method,[12] as shown in Table 1.

RESULTS AND DISCUSSION

Table 2 shows the pressure–composition (P–x) isotherms for the CO_2 + THF-A system at T = (313.15, 323.15, 333.15, 343.15, 353.15, and 363.15) K with pressures ranging from (5.19 to 17.29) MPa. Table 3 shows the pressure–composition (P–x) isotherms for the CO_2 + THFMA system at T = (313.15, 323.15, 333.15, 343.15, 353.15, and 363.15) K with pressures ranging from (5.28 to 17.70) MPa. The objective function (OBF) and the absolute average deviation of pressure (AADP) percent for the correlation were defined as follows.

$$\mathrm{OBF} = \sum_{i}^{N} \left| \frac{P_{\mathrm{exp}} - P_{\mathrm{cal}}}{P_{\mathrm{exp}}} \right| \tag{5}$$

$$\mathrm{AADP}(\%) = \frac{\sum_{i=1}^{N} |(P_{\mathrm{exp}} - P_{\mathrm{cal}})/P_{\mathrm{exp}}|}{N} \cdot 100 \tag{6}$$

where N is the number of experimental data points. P_{exp} and P_{cal} are the experimental and calculated pressures, respectively.

The binary interaction parameter k_{ij} and the AADP (%) for CO_2 + THF-A and CO_2 + THFMA are summarized in Table 4.

Figure 2 presents the comparisons between the experimental results for THF-A and the correlation data that were obtained with the critical constants using the Nannoolal–Rarey and Constantinou–Gani methods. Figure 3 shows the correlation results for CO_2 + THFMA obtained in the same way. In the case of both of these group contribution methods, there is no significant difference between the experimental results and correlation data. However, the Constantinou–Gani method shows a tendency to slightly overestimate (~0.7 MPa) the experimental values except in the case of THFMA at (353.15 and 363.15) K. The Nannoolal–Rarey method produced underestimated (~5 MPa) experimental results near the critical region. As a result, when we considered the correlation results of critical region and the AADP(%), the Constantinou–Gani method provides the best correlation in these systems.

CONCLUSION

We measured the pressure–composition (P–x) isotherms for binary mixtures of CO_2 + tetrahydrofurfuryl acrylate and CO_2 + tetrahydrofurfuryl methacrylate at temperatures ranging from (313.15 to 363.15) K and pressures of up to 18 MPa. The experimental results were correlated with the Peng–Robinson equation of state using the van der Waals one-fluid mixing rule using only one binary interaction parameter, k_{ij}. We used the Constantinou–Gani and Nannoolal–Rarey group contribution methods to estimate the critical constants (T_C, P_C). The acentric factor (ω) is estimated with the Lee–Kesler method. The correlated pressure data of THF-A were slightly overestimated (~0.7 MPa) and those of THFMA underestimated (~5 MPa) near the critical region. The Constantinou–Gani group contribution method and Lee–Kesler method produced the best correlation with the experimental data [AADP(%) = 1.91 (THF-A) and 2.59 (THFMA)].

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REFERENCES

(1) Howe-Grant, M.; Kroschwitz, J. I. *Encyclopedia of Chemical Technology*, supplement ed.; John Wiley & Sons: New York, 1998.

(2) Mangala, B.; Michael, B. Low shrinkage polymer/monomer mixtures for biomedical use. U.K. Patent Application GB2107341, 1983.

(3) Upson, D. A.; Steklenski, D. J. Vinyl acetate polymers and latex compositions containing same. U.S. Patent 4,544,723, 1983.

(4) Supercritical fluid extraction. http://en.wikipedia.org/wiki/Supercritical_fluid_extraction (accessed July 2011).

(5) Shin, J.; Lee, Y.-W.; Kim, H.; Bae, W. High-Pressure Phase Behavior of Carbon Dioxide + Heptadecafluorodecyl Acrylate + Poly(heptadecafluorodecyl acrylate) System. *J. Chem. Eng. Data* **2006**, *51* (5), 1571–1575.

(6) Kwon, S.; Bae, W.; Kim, H. High-Pressure Phase Behavior of CO_2 + *N*-Vinyl Caprolactam and CO_2 + *N*-Methyl Caprolactam Systems. *J. Chem. Eng. Data* **2005**, *50* (5), 1560–1563.

(7) Bae, W.; Kwon, S.; Byun, H.-S.; Kim, H. Phase behavior of the poly(vinyl pyrrolidone) + *N*-vinyl-2-pyrrolidone + carbon dioxide system. *J. Supercrit. Fluids* **2004**, *30* (2), 127–137.

(8) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15* (1), 59–64.

(9) Lee, B. I.; Kesler, M. G. A generalized thermodynamic correlation based on three-parameter corresponding states. *AIChE J.* **1975**, *21* (3), 510–527.

(10) Nannoolal, Y.; Rarey, J.; Ramjugernath, D.; Cordes, W. Estimation of pure component properties: Part 1. Estimation of the normal boiling point of non-electrolyte organic compounds via group contributions and group interactions. *Fluid Phase Equilib.* **2004**, *226*, 45–63.

(11) Nannoolal, Y.; Rarey, J.; Ramjugernath, D. Estimation of pure component properties: Part 2. Estimation of critical property data by group contribution. *Fluid Phase Equilib.* **2007**, *252* (1—2), 1–27.

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

(13) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill Book Company: New York, 2000.