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High-Pressure Phase Behavior of Methyl Lactate and Ethyl Lactate in Supercritical Carbon Dioxide

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ABSTRACT: Lactates obtained from biological sources are used as solvents in various industries from fine chemicals to pharmaceuticals. However, chemicals dissolved in lactates are typically degenerated during distillation due to the high boiling point of lactates. This problem can be solved by supercritical fluid extraction (SCFE) at lower temperatures instead of distillation. SCFE requires high-pressure phase behavior data on CO_2 and lactates for its design and operation. The high-pressure phase behavior of methyl lactate and ethyl lactate in CO_2 was measured from (323.2 to 363.2) K using a variable-volume view cell apparatus. Experimental data were well-correlated by the Peng−Robinson equation of state (PR EOS) using the Wong−Sandler mixing rules and the nonrandom two-liquid (NRTL) model. The critical constants were estimated by the Nannoolal−Rarey method, and the acentric factor was estimated by the Lee−Kesler method.

INTRODUCTION

Lactates made from biological sources are an attractive subject of research due to their interesting chemical properties. Lactates have low toxicity and high boiling points,[1] along with the ability to dissolve organic compounds such as nitro and ethyl cellulose, gums, oils, dyes, synthesis polymers, and paints.[2] Many have tried to apply these innate properties of lactates to the development of a solvent capable of being utilized in various industries. Their potential for wide application and good solvent properties make lactates ideal candidates to replace halogenated solvents such as ozone-depleting chlorofluorocarbons (CFCs), carcinogenic methylene chloride, toxic ethylene glycol ethers, and chloroform.[1]

Despite their desirable physical and chemical properties, the removal of lactates by separation processes such as distillation and liquid−liquid extraction has proven to be difficult. Specifically, distillation can alter or degenerate products due to the typical high boiling points of lactates. Further, liquid−liquid extraction cannot be performed since lactates mix too well with general solvents. These separation problems can be solved, however, with supercritical fluid extraction (SCFE) using supercritical carbon dioxide ($scCO_2$), which is inexpensive, nonflammable, and nontoxic.[3]

To design and operate the SCFE process, experimental data are required. Particularly, high pressure phase equilibrium data containing $scCO_2$ are required for plant design as well as wider industrial applications. In this study, we measured the pressure−composition ($P-x$) isotherms for binary mixtures consisting of CO_2 + methyl lactate and CO_2 + ethyl lactate. Experimental data were obtained by a static method using a variable-volume view cell in CO_2 at temperatures from (323.2 to 363.2) K. The experimental data were correlated by the Peng−Robinson equation of state (PR-EOS)[4] using the van der Waals one-fluid mixing rule and the Wong−Sandler mixing rule.[5] The critical properties were estimated by Nannoolal−Rarey method,[6,7] whereas the acentric factor was estimated by the Lee−Kesler method.[8]

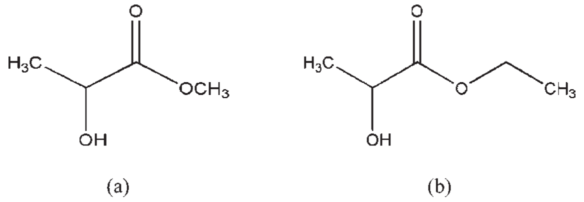

Figure 1. Chemical structure of (a) methyl lactate and (b) ethyl lactate.

EXPERIMENTAL SECTION

Materials. Methyl lactate (CAS No. 547-64-8, min. 97 %) and ethyl lactate (CAS No. 97-64-3, min. 98 %) were obtained from Tokyo Chemical Industry and used without further purification. Carbon dioxide (purity: min. 99.999 %) was purchased from Korea Industrial Gases. Verification of the purity of the chemicals was tested. Figure 1 shows the chemical structure of methyl lactate and ethyl lactate.

Apparatus and Procedure. Figure 2 shows the experimental apparatus used for obtaining the bubble points, critical points, or dew points of CO_2 + lactate binary mixture systems. This

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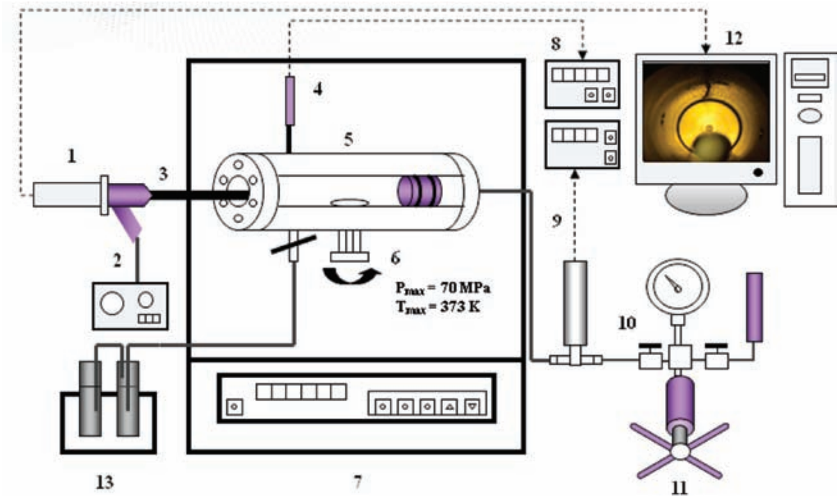

Figure 2. Schematic diagram of the experimental apparatus; (1) camera, (2) light source, (3) boroscope, (4) thermocouple, (6) magnetic stirrer, (7) air bath, (8) digital thermometer, (9) digital pressure transducer, (10) pressure gauge, (11) hand pump, (12) computer monitor, and (13) trap.

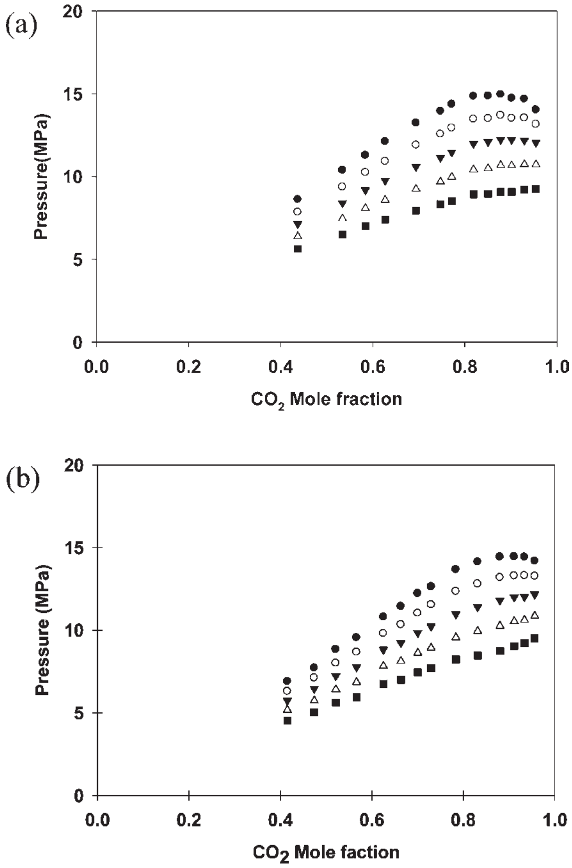

Figure 3. High-pressure phase behavior measurement result of the (a) CO_2 + methyl lactate and (b) CO_2 + ethyl lactate binary mixture systems at ●, 363.2 K; ○, 353.2 K; ▼, 343.2 K; △, 333.2 K; ■, 323.2 K.

apparatus has been described in detail elsewhere.[9] Several high-pressure phase behavior data which were acquired from this experiment were reported.[10−12] The experimental system consisted of a variable-volume cell, a high pressure generator, and a visual apparatus. The view cell was made of high nickel-content austenitic steel (5.7 cm outer diameter (OD), 1.59 cm inner diameter (ID), ~ 25 cm^3 working volume, fitted with a 1.9 cm OD, 1.3 cm thick sapphire window). The CO_2 + lactate systems were typically studied by the following experimental procedures. The cell was initially purged twice with nitrogen and CO_2 at room temperature to remove all chemicals and traces of air. A designed amount of methyl lactate or ethyl lactate was then loaded into the cell using a syringe to within ± 0.001 g. This was followed by the injection of a designed weight of CO_2 into the cell to within ± 0.01 g using a high-pressure bomb. The CO_2 + methyl lactate or ethyl lactate mixture in the cell was compressed to the desired operating pressure by a movable piston within the cell using high-pressure water provided by a pressure generator (High Pressure Equipment Co., model 62-6-10). A magnetic stirring bar in the cell was used to promote mixture equilibrium. The pressure of the solution was monitored by a water pressure indicator (Paroscientific Inc., model no. 730). The temperature was measured using a PRT type thermometer (Hart Scientific Inc., model 5622-32SR, accuracy of ± 0.045 K) fixed to the surface of the cell and displayed by an indicator (Hart Scientific Inc., model 1502). Calibration of the pressure transducer and thermometer was done by Korea Testing Laboratory (KTL), a national calibration laboratory. The calibration certificate of KTL reported that the uncertainty of the thermometer was 0.022 K, while that of the pressure transducer was 0.002 MPa.

The temperature of the cell was maintained to within ± 0.1 K and measured to within ± 0.1 K. The mixture in the cell was compressed at a fixed temperature and high-pressure to a single phase. The pressure was then slowly decreased until the bubble, critical, or dew point appeared. This procedure was repeated several times until fluctuations in phase transition pressure were minimized to within 0.03 MPa. Internal images were projected onto a computer monitor using a camera (Veltk International, Inc., model CVC5220) and a boroscope (Olympus Corp., model R100-0328-000-50) set toward a sapphire window.

■ THERMODYNAMIC MODELS

In this study, the experimental data were correlated with the PR-EOS[4] using the van der Waals one-fluid mixing rule and the Wong−Sandler mixing rules.[5]

Table 1. Experimental Data for the CO_2 + Methyl Lactate Binary Mixture System

T/K	P/MPa	mole fraction of CO_2	transition[a]	σ_P[b]
363.2	8.62	0.437	BP	0.004
363.2	10.40	0.534	BP	0.007
363.2	11.29	0.584	BP	0.001
363.2	12.12	0.627	BP	0.005
363.2	13.24	0.694	BP	0.007
363.2	13.96	0.747	BP	0.006
363.2	14.38	0.771	BP	0.011
363.2	14.86	0.819	BP	0.017
363.2	14.88	0.850	CP	0.008
363.2	14.96	0.878	DP	0.008
363.2	14.74	0.901	DP	0.011
363.2	14.70	0.929	DP	0.012
363.2	14.03	0.954	DP	0.002
353.2	7.86	0.437	BP	0.009
353.2	9.38	0.534	BP	0.002
353.2	10.25	0.584	BP	0.022
353.2	10.93	0.627	BP	0.013
353.2	11.91	0.694	BP	0.013
353.2	12.58	0.747	BP	0.002
353.2	12.95	0.771	BP	0.002
353.2	13.49	0.819	CP	0.001
353.2	13.52	0.850	DP	0.007
353.2	13.70	0.878	DP	0.014
353.2	13.53	0.901	DP	0.012
353.2	13.55	0.929	DP	0.001
353.2	13.16	0.954	DP	0.012
343.2	7.14	0.437	BP	0.003
343.2	8.41	0.534	BP	0.001
343.2	9.19	0.584	BP	0.005
343.2	9.76	0.627	BP	0.004
343.2	10.60	0.694	BP	0.024
343.2	11.14	0.747	BP	0.003
343.2	11.47	0.771	BP	0.005
343.2	11.99	0.819	BP	0.002
343.2	12.11	0.850	BP	0.011
343.2	12.23	0.878	CP	0.008
343.2	12.22	0.901	DP	0.012
343.2	12.19	0.929	DP	0.002
343.2	12.06	0.954	DP	0.006
333.2	6.38	0.437	BP	0.003
333.2	7.45	0.534	BP	0.002
333.2	8.09	0.584	BP	0.001
333.2	8.59	0.627	BP	0.005
333.2	9.25	0.694	BP	0.006
333.2	9.69	0.747	BP	0.004
333.2	9.97	0.771	BP	0.005
333.2	10.42	0.819	BP	0.008
333.2	10.49	0.850	BP	0.001
333.2	10.68	0.878	BP	0.013
333.2	10.67	0.901	BP	0.007
333.2	10.73	0.929	CP	0.002
333.2	10.72	0.954	DP	0.016
323.2	5.63	0.437	BP	0.002
323.2	6.51	0.534	BP	0.009
323.2	6.99	0.584	BP	0.010
323.2	7.40	0.627	BP	0.006
323.2	7.95	0.694	BP	0.005
323.2	8.33	0.747	BP	0.005
323.2	8.50	0.771	BP	0.001
323.2	8.93	0.819	BP	0.012
323.2	8.95	0.850	BP	0.002
323.2	9.08	0.878	BP	0.005
323.2	9.08	0.901	BP	0.008
323.2	9.21	0.929	BP	0.010
323.2	9.26	0.954	CP	0.008

[a] BP: bubble point, CP: critical point, DP: dew point. [b] Standard deviation of pressure, $\sigma_P = [(\Sigma_{k=1}^{n}(P_k - P_{\text{aver}})^2)/(n)]^{1/2}$.

The PR-EOS is expressed as follows;

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

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

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

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

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

where T_c is the critical temperature, p_c is the critical pressure, T_r is the reduced temperature, and ω is the acentric factor.

The van der Waals one-fluid mixing rules used in this study are given by

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

$$b = \sum_i x_i b_i \tag{7}$$

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{8}$$

where k_{ij} is the binary interaction parameter.

The Wong−Sandler mixing rule is represented as

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT}} \tag{9}$$

$$a_m = b_m\left(\sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C}\right) \tag{10}$$

Table 2. Experimental Data for the CO_2 + Ethyl Lactate Binary Mixture System

T/K	P/MPa	mole fraction of CO_2	transition[a]	σ_P[b]
363.2	6.91	0.415	BP	0.006
363.2	7.72	0.474	BP	0.002
363.2	8.84	0.521	BP	0.003
363.2	9.55	0.566	BP	0.001
363.2	10.81	0.625	BP	0.008
363.2	11.44	0.664	BP	0.003
363.2	12.23	0.700	BP	0.007
363.2	12.64	0.730	BP	0.003
363.2	13.67	0.784	BP	0.010
363.2	14.14	0.831	BP	0.003
363.2	14.44	0.880	CP	0.012
363.2	14.45	0.911	DP	0.006
363.2	14.43	0.934	DP	0.005
363.2	14.20	0.956	DP	0.011
353.2	6.31	0.415	BP	0.008
353.2	7.12	0.474	BP	0.012
353.2	8.01	0.521	BP	0.009
353.2	8.68	0.566	BP	0.017
353.2	9.80	0.625	BP	0.004
353.2	10.35	0.664	BP	0.006
353.2	11.03	0.700	BP	0.006
353.2	11.54	0.730	BP	0.017
353.2	12.35	0.784	BP	0.007
353.2	12.81	0.831	BP	0.001
353.2	13.20	0.880	CP	0.013
353.2	13.29	0.911	DP	0.002
353.2	13.30	0.934	DP	0.010
353.2	13.27	0.956	DP	0.011
343.2	5.74	0.415	BP	0.007
343.2	6.46	0.474	BP	0.005
343.2	7.23	0.521	BP	0.010
343.2	7.76	0.566	BP	0.008
343.2	8.82	0.625	BP	0.014
343.2	9.23	0.664	BP	0.001
343.2	9.84	0.700	BP	0.004
343.2	10.23	0.730	BP	0.009
343.2	10.97	0.784	BP	0.010
343.2	11.40	0.831	BP	0.002
343.2	11.80	0.880	BP	0.004
343.2	11.99	0.911	CP	0.018
343.2	12.02	0.934	DP	0.004
343.2	12.17	0.956	DP	0.008
333.2	5.17	0.415	BP	0.015
333.2	5.73	0.474	BP	0.006
333.2	6.41	0.521	BP	0.003
333.2	6.86	0.566	BP	0.013
333.2	7.82	0.625	BP	0.001
333.2	8.12	0.664	BP	0.012
333.2	8.62	0.700	BP	0.007
333.2	8.93	0.730	BP	0.011
333.2	9.55	0.784	BP	0.002
333.2	9.94	0.831	BP	0.007
333.2	10.26	0.880	BP	0.005

Table 2. Continued

T/K	P/MPa	mole fraction of CO_2	transition[a]	σ_P[b]
333.2	10.53	0.911	CP	0.000
333.2	10.62	0.934	DP	0.005
333.2	10.86	0.956	DP	0.008
323.2	4.54	0.415	BP	0.007
323.2	5.03	0.474	BP	0.008
323.2	5.62	0.521	BP	0.002
323.2	5.95	0.566	BP	0.011
323.2	6.75	0.625	BP	0.004
323.2	7.00	0.664	BP	0.004
323.2	7.45	0.700	BP	0.009
323.2	7.70	0.730	BP	0.007
323.2	8.22	0.784	BP	0.004
323.2	8.47	0.831	BP	0.008
323.2	8.75	0.880	BP	0.018
323.2	9.03	0.911	BP	0.002
323.2	9.20	0.934	BP	0.004
323.2	9.51	0.956	CP	0.004

[a] BP: bubble point, CP: critical point, DP: dew point. [b] Standard deviation of pressure, $\sigma_P = [(\sum_{k=1}^{n}(P_k - P_{\text{aver}})^2)/(n)]^{1/2}$.

$$\left(b-\frac{a}{RT}\right)_{ij} = \frac{\left(b_i-\frac{a_i}{RT}\right)+\left(b_j-\frac{a_j}{RT}\right)}{2}(1-k_{ij}) \qquad (11)$$

where $C = \ln[(2^{1/2}) - 1]/(2^{1/2})$ for the PR-EOS. Since the excess Helmholtz free energy of mixing at infinite pressure is assumed equal to the excess Gibbs free energy (G^E) at low pressure, the G^E model is used in place of A_∞^E. We selected the NRTL (nonrandom two-liquid) model[13] as an activity coefficient model in this study.

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_i x_i \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \qquad (12)$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \qquad \alpha_{ij} = \alpha_{ji} \qquad (13)$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \qquad \Delta g_{ij} = g_{ij} - g_{jj} \qquad (14)$$

where τ_{ij} and τ_{ji} are the interaction parameters and α_{ij} is the nonrandomness parameter. The nonrandomness parameter α_{ij} was fixed on 0.3.

To correlate experimental data with the PR-EOS, it was necessary to include the critical properties (T_c, P_c) and acentric factor (ω) of the pure component. Since there are no experimental data describing the critical properties of methyl lactate and ethyl lactate, T_c and P_c were estimated using the group contribution method. Critical properties were estimated by the Nannoolal–Rarey method, whereas the acentric factor was estimated by the Lee–Kesler method.

■ RESULTS AND DISCUSSION

Figure 3, Table 1, and Table 2 show the pressure–composition (P–x) isotherms for the CO_2 + methyl lactate and CO_2 + ethyl

Table 3. Critical Constants and Acentric Factor for the PR-EOS

	T_c/K	P_c/MPa	ω	remark
CO_2	304.2	7.38	0.225	*a*
methyl lactate	629.5	3.71	0.312	*b*
ethyl lactate	633	3.34	0.348	*b*

[a] Reference 14. [b] Estimated with the Nannoolal−Rarey method and Lee−Kesler method.[7,8]

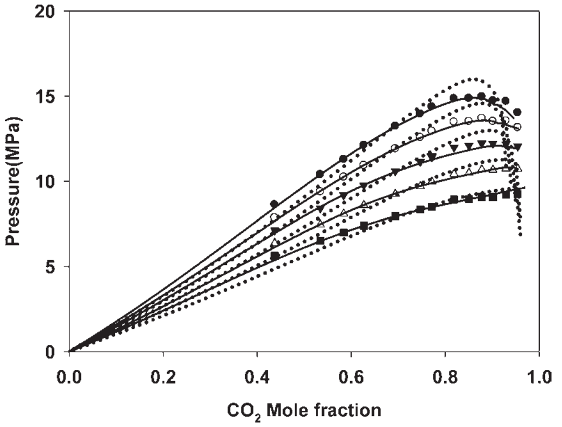

Figure 4. Results correlated using the PR-EOS with the van der Waals one-fluid mixing rule (vdW, dotted line) and Wong−Sandler mixing rule (WS, solid line) for the CO_2 + methyl lactate system at ●, 363.2 K; ○, 353.2 K; ▼, 343.2 K; △, 333.2 K; ■, 323.2 K.

lactate systems at T = (323.2, 333.2, 343.2, 353.2, and 363.2) K, and at pressures ranging from (5 to 15) MPa.

The correlation of the experimental data with the PR-EOS requires the critical constants and acentric factor (ω). The Nannoolal−Rarey group contribution method for the estimation of critical temperature requires the normal boiling point. The experimental and normal boiling points (T_b) of methyl lactate and ethyl lactate were used as listed by Tokyo Chemical Industry Co., Ltd. catalog. The estimation results of the critical constants and the acentric factor are shown in Table 3.

The simplex algorithm was used to determine k_{ij}, the only binary interaction parameter used in this work. The objective function (OBF) and the percentage of absolute average deviation of pressure (AADP) for the correlation were defined by:

$$\mathrm{OBF} = \sum_{i=1}^{N} \left| \frac{P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}}}{P_i^{\mathrm{exp}}} \right| \tag{15}$$

$$\mathrm{AADP}(\%) = \frac{\sum_{i=1}^{N} \left| \frac{P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}}}{P_i^{\mathrm{exp}}} \right|}{N} \cdot 100 \tag{16}$$

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

The experimental data for carbon dioxide + methyl lactate and carbon dioxide + ethyl lactate systems were correlated by the PR-EOS with the van der Waals one-fluid mixing rule and Wong−Sandler mixing rule. As shown in Figures 4 and 5, the van der Waals one-fluid mixing rule overestimated near the critical regions of both systems. However, the Wong−Sandler mixing rule underestimated near the critical regions of both systems.

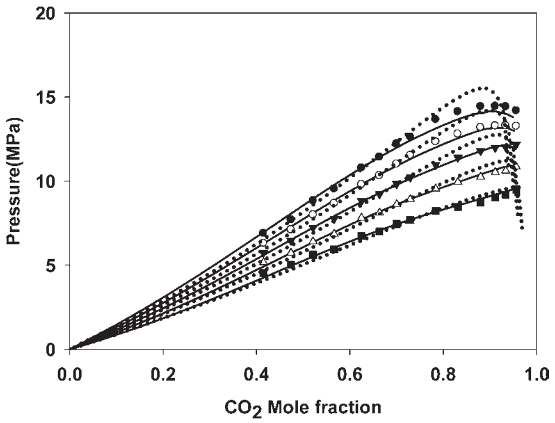

Figure 5. Results correlated using the PR-EOS with the van der Waals one-fluid mixing rule (vdW, dotted line) and Wong−Sandler mixing rule (WS, solid line) for the CO_2 + ethyl lactate system at ●, 363.2 K; ○, 353.2 K; ▼, 343.2 K; △, 333.2 K; ■, 323.2 K.

Table 4. Correlation Results for CO_2 + Methyl Lactate and CO_2 + Ethyl Lactate Using the PR-EOS with van der Waals One-Fluid (vdW) Mixing Rule and Wong−Sandler (WS) Mixing Rule

	PR-vdW		PR-WS			
	k_{ij}	AADP (%)	k_{ij}	$\Delta g_{ij}/R$	$\Delta g_{ji}/R$	AADP (%)
CO_2 + methyl lactate	0.0709	5.77	0.5743	826.18	−189.97	1.01
CO_2 + ethyl lactate	0.0526	4.52	0.5847	928.06	−304.34	1.21

The binary interaction parameters for these systems are summarized in Table 4 together with AADP (%). While the PR-EOS with van der Waals one-fluid mixing rule fitted within 5.77 % and 4.52 % AADP for carbon dioxide + methyl lactate and carbon dioxide + ethyl lactate systems, respectively, the PR-EOS with Wong−Sandler mixing rule correlated well them within 1.01 % and 1.21 % AADP for both systems, respectively. The PR-EOS with Wong−Sandler mixing had better calculated results than that with van der Waals one-fluid mixing rule in both systems. Especially, the Wong−Sandler mixing rule makes a more accurate estimation near the critical region than the van der Waals one-fluid mixing rule. For the correct prediction of the complex binary mixture systems, such as CO_2 + methyl lactate and CO_2 + ethyl lactate systems, the cubic equation of state needs more complex mixing rules, such as the Wong−Sandler mixing rule.

■ CONCLUSION

The pressure−composition (P−x) isotherms for the binary mixtures of CO_2 + methyl lactate and CO_2 + ethyl lactate were measured using a synthetic method comprised of a variable-volume view cell at temperatures ranging from (323.2 to 363.2) K and pressures up to 15 MPa. The experimental data were correlated by the PR-EOS using van der Waals one-fluid mixing rule and the Wong−Sandler mixing rule. The Nannoolal−Rarey method and the Lee−Kesler method were used for the pure component parameters. The PR-EOS with Wong−Sandler mixing shows the better calculated results than that with van der Waals one-fluid mixing rule, so PR-EOS need more complex mixing rules such as the Wong−Sandler mixing rule in CO_2 + methyl lactate and CO_2 + ethyl lactate systems.

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