Vapor−Liquid Equilibrium for Carbon Dioxide + Isopropyl, Isobutyl, and Isoamyl Acetates

Cheong Hoon Kwon, Myung Do Seo, Seung Wook Kim, Chul Soo Lee, and Jeong Won Kang*

Department of Chemical and Biological Engineering, Korea University, 5-Ga Anam-Dong, Sungbuk-Ku, Seoul 136-701, South Korea

Vapor−liquid equilibrium of three acetates (isopropyl, isobutyl, and isoamyl acetate) + carbon dioxide were measured using a circulating-type equilibrium cell at temperature ranging from (313.2 to 333.2) K and pressure up to 10 MPa. The measured experimental data were correlated by the Peng−Robinson with conventional mixing rule and nonrandom lattice fluid with hydrogen bonding equations of state with a single binary interaction parameter.

Introduction

Acetates are used in various fields of chemical and biological engineering such as food, cosmetic, and pharmaceutical industries. Recently, the production of acetates using enzymes in supercritical fluids[1] has emerged as an alternative to the conventional metal-catalyzed synthesis processes. Vapor−liquid equilibrium (VLE) data and reaction kinetic data are important to understand such processes. Several VLE results for CO_2 + acetates were published in the literature,[2−9] but the amount of data is still small. To the best of our knowledge,[2−9] the equilibrium data for carbon dioxide and isobutyl acetate system have not been reported. In this work, isothermal VLE data for three binary systems consisting of carbon dioxide with isopropyl acetate, isobutyl acetate, and isoamyl acetate at high pressure were measured using a circulating-type experimental apparatus. The experiments were carried out at temperatures ranging from (313.2 to 333.2) K and pressures ranging up to 10 MPa. The experimental results were correlated with the Peng−Robinson (PR) equation of state (EoS)[10] and nonrandom lattice fluid theory with hydrogen-bonding (NLF-HB) EoS.[11−14]

Experimental Section

Chemicals. Liquefied carbon dioxide with purity greater than 99.9 % was purchased from PS Chemical Co. (Seoul, South Korea) for use. The source and properties of the pure esters are summarized in Table 1. All chemicals were used without further purification.

Apparatus. The densities of the pure compounds at 298.2 K were measured using a DMA 5000 density meter (Anton Paar GmbH, Germany) with an uncertainty of $\pm$ 1.0 $\times$ 10^{-5} g·cm^{-3}. The measured densities agree reasonably well with the literature values except for the density of isopropyl acetate (difference: 0.002 g·cm^{-3}). A schematic diagram of the experimental apparatus used in this work is shown in Figure 1. The apparatus consists of three major parts: the high-pressure equilibrium cell, the sample injection and sampling part, and the gas chromatography for determining the compositions of the equilibrium phases. The high-pressure equilibrium cell in Figure 1 is made of stainless steel and has an internal volume of 150 mL. The equilibrium pressure was measured by means of a pressure gauge (Cole-Palmer Inc.) with a digital indicator (range (0 to 20) MPa; resolution: 0.001 MPa; uncertainty: $\pm$ 0.05 %; model

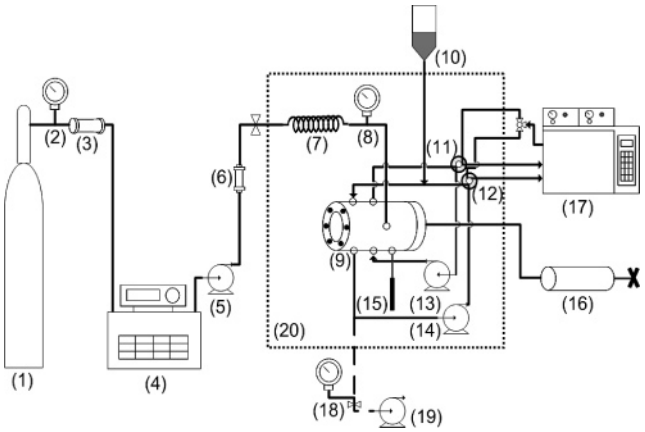

Figure 1. Schematic diagram of the experimental phase equilibrium apparatus: 1, CO_2 gas cylinder; 2, pressure gauge; 3, filter; 4, chiller; 5, high-pressure pump; 6, check valve; 7, preheater; 8, pressure transducer; 9, equilibrium cell; 10, liquid reservoir; 11, vapor sampling valve; 12, liquid sampling valve; 13, vapor circulation pump; 14, liquid circulation pump; 15, thermocouple; 16, hand pump; 17, gas chromatograph; 18, vacuum pressure gauge; 19, vacuum pump; 20, air bath.

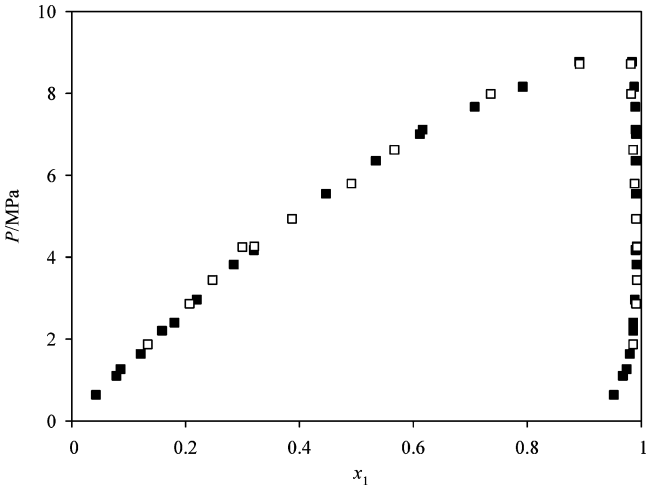

Figure 2. Comparison of the VLE measurement results for carbon dioxide (1) + toluene (2) system with the literature data at 323.2 K: □, this work; ■, literature data.[16]

* Corresponding author. Tel.: +82-2-3290-3305. Fax: +82-2-926-6102. E-mail: jwkang@korea.ac.kr.

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Table 1. Properties of Chemicals Used in This Study

chemical	supplier	100 *w*	ρ/g·cm^{-3} at 298.15 K this work	ρ/g·cm^{-3} at 298.15 K literature data[15]
isopropyl acetate	Aldrich Chemical Co.	>99.0 %	0.8691	0.8711
isobutyl acetate	Aldrich Chemical Co.	>99.0 %	0.8692	0.8695
isoamyl acetate	Sigma-Aldrich, Inc.	>98.0 %	0.8669	0.8666

Table 2. Vapor−Liquid Equilibrium Data for CO_2 (1) + Toluene (2) System at 323.2 K

P/MPa	x_1	y_1	*P*/MPa	x_1	y_1
1.87	0.133	0.986	4.94	0.387	0.991
2.87	0.216	0.991	5.80	0.491	0.989
3.45	0.247	0.992	6.62	0.567	0.986
4.25	0.300	0.992	7.99	0.736	0.983
4.27	0.321	0.992	8.72	0.892	0.982

Table 3. Vapor−Liquid Equilibrium Data for CO_2 (1) + Isopropyl Acetate (2)

T = 313.2 K			T = 323.2 K			T = 333.2 K		
P/MPa	x_1	y_1	*P*/MPa	x_1	y_1	*P*/MPa	x_1	y_1
1.65	0.424	0.983	1.05	0.258	0.980	2.39	0.435	0.989
2.16	0.502	0.991	1.54	0.354	0.985	2.81	0.491	0.990
2.73	0.607	0.995	2.56	0.516	0.991	2.94	0.509	0.990
2.94	0.635	0.996	3.04	0.580	0.993	3.52	0.576	0.988
4.32	0.771	0.997	4.28	0.703	0.995	3.70	0.596	0.987
4.38	0.778	0.997	4.42	0.718	0.995	4.52	0.670	0.983
5.71	0.872	0.997	5.22	0.779	0.995	5.78	0.755	0.979
5.91	0.883	0.997	6.07	0.834	0.995	6.42	0.795	0.983
6.65	0.934	0.997	6.52	0.859	0.995	6.56	0.805	0.985
7.25	0.984	0.996	7.56	0.918	0.997	8.71	0.914	0.999

Table 4. Vapor−Liquid Equilibrium Data for CO_2 (1) + Isobutyl Acetate (2)

T = 313.2 K			T = 323.2 K			T = 333.2 K		
P/MPa	x_1	y_1	*P*/MPa	x_1	y_1	*P*/MPa	x_1	y_1
1.30	0.292	0.990	1.77	0.328	0.995	1.12	0.202	0.989
1.57	0.341	0.992	1.79	0.332	0.994	1.46	0.255	0.989
2.36	0.471	0.996	2.41	0.429	0.993	2.15	0.350	0.989
2.89	0.546	0.996	2.88	0.495	0.990	3.25	0.481	0.988
4.23	0.707	0.994	3.00	0.509	0.989	3.53	0.513	0.985
4.54	0.738	0.995	4.43	0.664	0.995	3.91	0.552	0.991
6.10	0.869	0.996	4.44	0.663	0.994	4.66	0.622	0.990
6.12	0.870	0.998	5.82	0.777	1.000	6.06	0.731	0.994
6.77	0.914	0.997	7.93	0.912	0.993	6.48	0.759	0.995
7.57	0.962	1.000	8.27	0.934	0.988	8.53	0.884	1.000

SM-210, Instech Laboratories Inc.). The temperature was controlled within ± 0.5 K using a PID controller (UT-48, UConTec, South Korea) with a forced-convection air bath. The temperature in the equilibrium cell was measured using a K-type thermocouple with uncertainty of ± 0.1 K. Liquefied carbon dioxide was fed by a liquid pump (Eldex Laboratories, Inc., USA). The vapor and liquid phases were circulated using a recirculation pump (Duplex metering pump, Eldex Laboratories, Inc., USA) until the system reached the equilibrium.

Vapor and liquid samples were taken by means of sampling valves (Rheodyne L.P., Rohnert Park, CA) and analyzed by an online gas chromatograph (GC; Donam Instrument Inc., Seoul, South Korea). The vapor and liquid sampling valves have external loops with volumes of (20 and 1) μL, respectively. A GC with a thermal conductivity detector (TCD) and a Carbowax column (length 1.83 m, i.d. 2.159 mm, and o.d. 3.175 mm) was used to analyze the equilibrium compositions. The GC was calibrated using the absolute method, and the consistencies of the GC calibration curves were checked by comparing the peaks of known amount. The uncertainty of the equilibrium compositions was estimated to be ± 0.002 mole fraction. Helium with a flow rate of 20 mL·min^{-1} was used as the carrier gas. The injector and detector temperatures were both kept at 453.2 K. The temperature of the column of the GC was kept at 343.2 K for CO_2 + isopropyl acetate, at 377.2 K for CO_2 + isobutyl acetate, and at 353.2 K for CO_2 + isoamyl acetate in order to separate the CO_2 and acetates effectively.

Table 5. Vapor−Liquid Equilibrium Data of CO_2 (1) + Isoamyl Acetate (2)

T = 313.2 K			T = 323.2 K			T = 333.2 K		
P/MPa	x_1	y_1	*P*/MPa	x_1	y_1	*P*/MPa	x_1	y_1
1.74	0.311	0.994	1.91	0.301	0.995	1.51	0.203	0.991
1.87	0.329	0.995	2.17	0.337	0.995	2.07	0.278	0.990
3.08	0.490	0.998	3.45	0.494	0.997	2.88	0.379	0.994
3.38	0.527	0.998	3.69	0.524	0.996	3.75	0.481	0.987
4.20	0.630	0.999	4.98	0.646	0.994	4.16	0.515	0.993
4.85	0.707	0.999	5.04	0.645	0.996	4.42	0.564	0.994
5.65	0.784	0.999	6.11	0.739	0.998	4.91	0.600	0.997
5.94	0.814	0.999	6.98	0.805	0.997	5.25	0.627	0.995
6.67	0.876	0.998	7.13	0.811	0.997	7.17	0.778	1.000
7.69	0.940	0.997	8.31	0.883	1.000	8.88	0.865	0.998

Table 6. Critical Constants for the Components

chemical	MW	T_c/K	P_c/MPa	ω	ref
carbon dioxide	44.01	304.14	7.375	0.239	17
isopropyl acetate	102.13	538.00	3.580	0.355	6, 17
isobutyl acetate	116.16	561.00	3.160	0.455	17
isoamyl acetate	130.19	599.00	2.840	0.398	7, 8, 17

Experimental Procedure. The equilibrium cell was first evacuated using a vacuum pump, and acetates were injected into the system. Then liquefied carbon dioxide was fed into the cell using the high-pressure pump to obtain the desired pressure. The pressure of the system was finely adjusted using the hand pump. The liquid and vapor phases of the sample were recirculated through a metering pump at a flow rate of 9 mL·min^{-1} in order to obtain rapid equilibrium. The mixture was stirred well for about 3 h and then allowed to rest for at least 6 h to ensure equilibrium. After the equilibration period, the liquid and vapor phases were sampled and sent to the GC for composition analysis. Measurements were repeated more than three times, and the averaged value was taken as the final composition.

Experimental Data. To test the correct operation of the experimental apparatus, VLE data for the binary carbon dioxide and toluene system were measured and compared with the values available in the literature.[16] As shown in Figure 2, the reproducibility of the experimental results was found to be within ± 1.0 MPa and ± 3.0 × 10^{-4} mole fraction in the vapor phase in comparison with the reported literature data. Numerical values of VLE data for carbon dioxide + toluene are reported in Table 2. The phase equilibrium data for the carbon dioxide + acetate systems (isopropyl acetate, isobutyl acetate, and isoamyl acetate) were measured at temperatures of (313.2, 323.2, and 333.2) K and are reported in Tables 3 to 5.

Result and Discussion

The experimental data were correlated with the PR and NLF-HB EoS. The PR EoS is widely used for correlating high-pressure VLE, and critical constants are required for the calculation. The parameters for the PR EoS used in this study are summarized in Table 6. A simple classical mixing rule with one binary interaction parameter (k_{ij}) was used to correlate the VLE data:

$$a_m = \sum\sum \sqrt{a_i a_j}\, x_i x_j (1 - k_{ij}) \qquad (1)$$

The NLF EoS was first proposed by us[11,12] and has recently been extended to associating systems (NLF-HB).[13,14] The

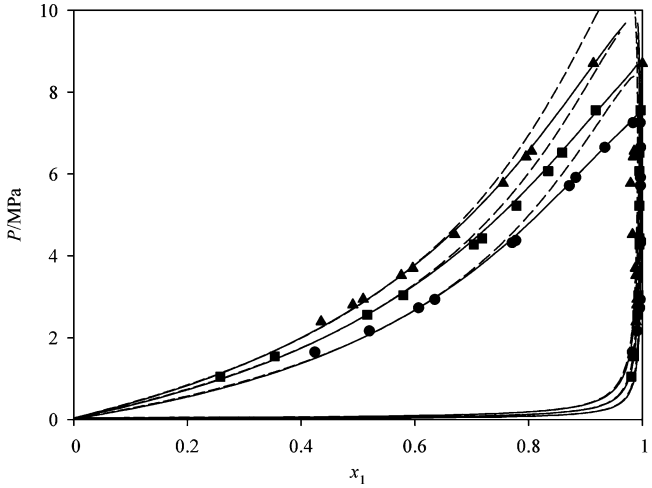

Figure 3. Comparison of measured data with correlated values using PR EoS and NLF-HB EoS for CO_2 (1) + isopropyl acetate (2): ■, experimental data at 313.2 K; ●, experimental data at 323.2 K; ▲, experimental data at 333.2 K; - - -, PR EoS calculations; —, NLF-HB EoS calculations.

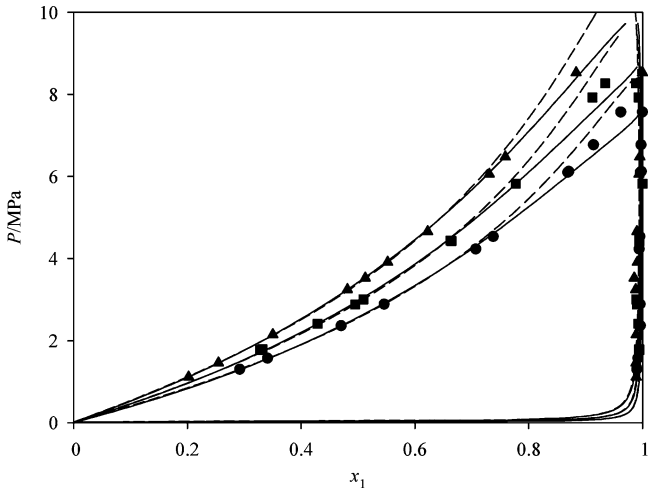

Figure 4. Comparison of measured data with correlated values using PR EoS and NLF-HB EoS for CO_2 (1) + isobutyl acetate (2): ■, experimental data at 313.2 K; ●, experimental data at 323.2 K; ▲, experimental data at 333.2 K; - - -, PR EoS calculations; —, NLF-HB EoS calculations.

proposed EoS has been compared with other well-known EoS models.[16] The equation of state can be written as

$$\frac{PV_{\mathrm{H}}}{RT} = \frac{z}{2}\ln\left[1 + \left(\frac{q_{\mathrm{M}}}{r_{\mathrm{M}}} - 1\right)\rho\right] - \ln(1-\rho) + \frac{z\beta}{2}\epsilon_{\mathrm{M}}\theta^2 \quad (2)$$

Detailed descriptions and notations of the NLF-HB EoS are given in previous papers.[13,14] In this study, the one-fluid mixing rule was used to correlate the VLE data:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}\,(1 - k_{ij}) \quad (3)$$

The pure component energy parameters were assumed as the following temperature-dependent function:

$$\epsilon_{ii}/k = (\epsilon_i^A/k) + (\epsilon_{ii}^B/k)(T - T_0) + (\epsilon_{ii}^C/k)(T\ln T_0/T + T - T_0) \quad T_0 = 298.15\ \mathrm{K} \quad (4)$$

In the original version of the EoS, temperature-dependent size parameters and energy parameters were used for the calculations. In this study, bulkiness parameters were considered as new parameters and temperature dependency of the size parameters were removed except for the supercritical component parameters. Bulkiness factors (l_i) can be introduced during the surface area calculation steps:

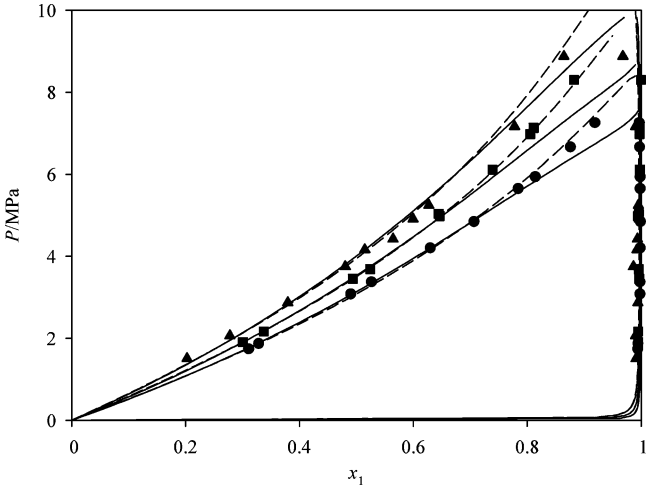

Figure 5. Comparison of measured data with correlated values using PR EoS and NLF-HB EoS for CO_2 (1) + isoamyl acetate (2): ■, experimental data at 313.2 K; ●, experimental data at 323.2 K; ▲, experimental data at 333.2 K; - - -, PR EoS calculations; —, NLF-HB EoS calculations.

Table 7. Pure Parameters for NLF-HB EoS

chemical	r_i	ϵ^{A}	ϵ^{B}	ϵ^{C}	l_i	range/K
carbon dioxide	2.6845	92.9964	−0.13698	−0.19458	−0.8	217 to 294
isopropyl acetate	7.8065	123.9271	−0.04601	−0.06042	−1.0	300 to 400
isobutyl acetate	8.7487	127.8233	−0.04703	−0.07026	0.0	300 to 400
isoamyl acetate	10.0096	130.0744	−0.05201	−0.05780	1.0	311 to 369

$$zq_i = r_i z - 2r_i + 2 - 2l_i \quad (5)$$

where z is the coordination number, q_i is the surface area, and r_i is segment length.

The lattice cell volume (v_{hs}) have been assumed to be temperature dependent as the following form:

$$v_{\mathrm{hs}}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = 8.7858 + 8.1711\exp\frac{-144.432}{T/\mathrm{K}} \quad (6)$$

With bulkiness factors introduced into the NLF-HB EoS, the temperature dependencies of size parameters are dampened and the size parameter (r_i) can be fitted as a constant. The energy and size parameters for carbon dioxide and esters used for the calculations are summarized in Table 7.

The optimum binary interaction parameters (k_{ij}) for PR EoS and NLF-HB EoS were determined to minimize the following objective function:

$$\mathrm{OBJF} = \sqrt{\Delta P^2 + \Delta y^2} = \sqrt{\left(\frac{1}{N_{\mathrm{data}}}\sum_i \frac{P_i^{\mathrm{exp}} - P_i^{\mathrm{cal}}}{P_i^{\mathrm{exp}}} \times 100\right)^2 + \left(\frac{1}{N_{\mathrm{data}}}\sum_i (y_i^{\mathrm{exp}} - y_i^{\mathrm{cal}}) \times 100\right)^2} \quad (7)$$

The calculation results are compared in Figures 3 to 5, and the numerical results are summarized in Table 8. PR EoS have differences in pressure ranging from (0.7 to 6.0) % and mole fraction error ranging from (0.1 to 6.0) %. The NLF-HB EoS has slightly smaller differences in pressure but larger differences in mole fractions. As discussed in a previous paper,[18] one cannot tell which model works better for supercritical VLE because uncertainties in the experimental measurement are relatively high

Table 8. Binary Interaction Parameters and Vapor−Liquid Equilibrium Calculation Results for PR EoS and NLF-HB EoS[a]

T	PR EoS			NLF-HB EoS		
K	k_{ij}	100 $\delta(P)$	100 $\delta(y)$	k_{ij}	100 $\delta(P)$	100 $\delta(y)$
			CO_2 + Isopropyl Acetate			
313.2	−0.16261	6.30	0.16	−0.08793	2.54	0.24
323.2	−0.14945	6.07	0.18	−0.07184	2.58	0.11
333.2	−0.16215	4.66	0.62	−0.07730	1.89	0.64
			CO_2 + Isobutyl Acetate			
313.2	−0.07113	3.17	0.20	−0.0257	1.90	0.25
323.2	−0.08070	3.21	0.29	−0.0264	2.22	0.39
333.2	−0.08355	1.83	0.37	−0.0286	0.60	0.39
			CO_2 + Isoamyl Acetate			
313.2	−0.01551	1.72	0.11	0.0140	1.99	0.16
323.2	−0.02336	0.72	0.19	0.0093	3.03	0.21
333.2	−0.03113	3.67	0.60	0.0055	3.79	0.79

[a] $\delta(P) = 1/N_{data}\sum_i|P_i^{exp} - P_i^{cal}/P_i^{exp}|$. $\delta(y) = 1/N_{data}\sum_i|y_i^{exp} - y_i^{cal}|$.

near the critical point and both models do not have proper consideration for abnormalities near critical points.

Conclusions

In this study, the isothermal VLE data for binary mixtures of carbon dioxide and various esters were measured at temperatures ranging from (313.2 to 333.2) K and pressures up to 10 MPa. The phase behavior of these binary experimental data was correlated with the PR EoS and the NLF-HB EoS with one adjustable binary interaction parameter. The fitted binary parameters are reported, and the correlations between the experimental and theoretical results are presented.

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